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STUDY OF AIR POLLUTANTS BY MICROWAVE SPECTROSCOPY

Contract No. CPA-22-69-144

Final Report

June, 1972

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The results and evaluations of experiments conducted to evaluate the usefulness of microwave spectroscopy as an analytical tool for air contamination studies are discussed. The background and theory as applied to analytical applications are presented. The following three possible analytical procedures are discussed in detail: 1) optimum power saturation method; 2) line areas; and 3) line intensities.

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SUMMARY

Background information and theory, particularly as they apply to analytical applications are presented. Three possible analytical procedures are discussed in some detail. These are the optimum power saturation method, line areas, and line intensities.

The optimum power method has the advantage that the problem of varying line widths is completely eliminated at pressures above some minimum value. It has two important disadvantages: (1) the power level must be optimized for each line and sample pressure encountered, and (2) the amount of power required is well beyond the capabilities of most microwave sources for most molecules. Provisions must be made to operate the crystal detector of the spectrometer so that its output is proportional to the square root of the applied power.

The line area is proportional to the partial pressure of an absorbing molecule and is also independent of the line width. It is however somewhat tedious to measure. We have shown that the product of the line height and the half power width has the same properties as the line area. Measurement is relatively quick and easy. A disadvantage of both area methods is that the scanning rate of the spectrometer must be uniform and repeatable. This was accomplished by locking the frequency of the source to a harmonic of a "tuned" crystal oscillator.

Direct quantitation by means of the line intensity is a very simple and adequate method for certain cases of interest. These include any system in which the desired component is in low concentrations and the composition of the bulk of the mixture is relatively constant. Trace components in air is an ideal system for this method.

The problem of adsorption of gases on the walls of the absorption cell is serious. The amount of such adsorption to be expected was shown by several experiments in which gas pressure was measured as a function of time. Equipment was assembled and a study conducted to determine whether the adsorption problem could be eliminated by a continuous flow-through system. The results indicated that strongly adsorbing compounds can be handled easier through preconditioning of a standard batch cell.

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I. INTRODUCTION

The purpose of the work supported by contract number CPA-22-69-144 was to evaluate the usefulness of microwave spectroscopy as an analytical tool for air contamination studies. For this type of work, an ideal analytical technique would (1) provide positive identification with little interference, (2) be applicable to a large range of compounds, (3) be suitable for good quantitative results, and (4) have high sensitivity. In addition, a desirable feature would be the ability to examine an air sample directly in the atmosphere, and at some distance from the particular analytical instrument.

Microwave spectroscopy obviously does not qualify 100% in all of the criteria given above. Its ability to provide a positive compound identification is certainly unexcelled by any known technique. In fact, the fundamental theory of microwave spectroscopy suggests the possibility that no future technique will be developed with a greater degree of compound specificity. In many cases, the identification by frequency of a single observed line in a sample is sufficient for compound identification. Finding two lines with matching frequencies and the proper intensity ratio for a compound is a good positive identification, while matching three lines to the spectrum of a given compound makes the identification an absolute certainty.

The number of compounds which have adequate microwave spectra is limited. The primary limitation is the requirement that a molecule must have a permanent dipole moment of reasonable value. Many molecules with small dipole moments have observable microwave spectra, but only with specialized techniques and very slow scans. The sensitivity for such compounds is generally too low for practical analytical applications. The dipole moment requirement is a necessary but not sufficient condition for a

molecule to have a useful microwave spectrum. Large molecules with many possible degrees of internal rotation have microwave spectra consisting of a very large number of weak lines. However, in spite of these limitations, a number of small molecules of interest to air contamination do have good microwave spectra.

The quantitative application of microwave spectroscopy has not been discussed extensively in the published literature. The quantitative handling of microwave spectral data is somewhat unique compared to other forms of molecular spectroscopy. For example, it is relatively easy to have too much source power in a microwave spectrometer and thereby produce line-broadening through power saturation. Line widths, and thus line intensities, are also quite sensitive to the types of molecular collisions which occur. The line width and intensity observed for a compound of fixed mole percentage in a gaseous mixture will vary with the nature of the other compounds which make up the mixture. Part of our work in this contract was to evaluate quantitative analytical methods using line heights directly, line heights under power saturation conditions, and line areas. A complete discussion of the advantages and disadvantages of these methods will be given later.

The theoretical sensitivity, or limits of detection, of a microwave spectrometer ranges from about 2 ppm for NH_3 to a more typical figure of 0.1 to 1.0 mole % as an average for a fairly representative collection of molecules. The figure of 2 ppm of NH_3 is based on a spectrometer capable of detecting an absorption line of intensity 10^{-9} cm^{-1}, and a line intensity of 1.5×10^{-4} cm^{-1} for the NH_3 24139 MHz line. A number of small molecules of interest have detection limits in the tens to hundreds of parts per million range.

Microwave spectroscopy is not useful for the direct observation of gaseous contaminants in the atmosphere. A microwave spectrometer normally operates at a pressure of 10 to 100 millitorr to keep the lines narrow. Increasing pressure produces line broadening, and at atmospheric pressure the lines have been broadened to the point where they can no longer be observed as discrete lines.

The main body of this report will be concerned with a discussion and evaluation of the experiments carried out under this contract. The evaluations will be done in terms of microwave spectroscopy as a practical quantitative analytical technique.

II. MICROWAVE SPECTROSCOPY BACKGROUND FOR ANALYTICAL APPLICATIONS

Microwave spectroscopy is the study of molecular processes which result in the absorption of electromagnetic energy in the frequency range of approximately 1000 MHz to 300,000 MHz. The principal molecular process which produces such absorption is the excitation of rotational levels of the molecule. Additional absorption lines result from the coupling of nuclear quadrupoles with rotational levels, internal rotation of one part of a molecule with respect to another part, rotational levels within excited vibrational states of a molecule, molecular inversion, very low energy vibrational states, and others. Fortunately, analytical applications of microwave spectroscopy do not depend upon a knowledge of the process or levels involved in producing a particular absorption line.

The application of microwave spectroscopy to qualitative identification problems does require a cataloging of all absorption lines observed in the spectrum of a compound. However, the identification of a reasonably pure compound requires only a knowledge of a few of the most intense lines in the spectrum of the compound. A search for minor components first requires that all small peaks associated with the already identified major components be identified and removed from consideration. Minor component identification then proceeds from the remaining peaks.

The rotational energy levels of a molecule are determined by the principal moments of inertia of that molecule. Thus, the rotational levels and absorption frequencies are defined by the masses of all atoms in a molecule and the geometric position of these atoms. A change in mass of an atom, e.g., by isotopic

substitution, will produce a major change in the frequencies of all lines in the spectrum of that molecule. A change in geometrical arrangement of atoms within a molecule, such as cis- and trans-isomers, also results in a major change in all frequencies in the microwave spectrum. The dependence of absorption frequencies on the molecular moments of inertia makes it essentially impossible for two molecules to have identical spectra. This condition reduces, but does not eliminate the possibility that two compounds may have absorption lines of the same frequency. The unique spectra plus inherently high resolution of a microwave spectrometer give microwave spectroscopy the ability to make an unambiguous compound identification.

A fundamental requirement for the observation of microwave spectra is that the molecule must possess a permanent dipole moment. Molecules such as methane, benzene, CCl_4, and N_2 cannot be observed. Many molecules which produce good infrared spectra from an oscillating bond moment, e.g., H-C-C-H or N-C-C-N, have no microwave spectra because of the lack of a permanent molecular dipole moment. The intensities of the spectra of geometric isomers may be quite different because of differences in the values of the permanent dipole moments of the two isomers. For example, the <u>cis</u> form of 1.2 difluoroethylene has a relatively intense spectrum, while the spectrum of the trans form is quite weak.

An understanding of the effects of gas pressure and microwave power on line intensities and shape are essential to quantitative applications of microwave spectroscopy. The very small energies involved and the ability of a microwave spectrometer to observe the effects of such small energy changes makes microwave absorption lines very sensitive to these effects.

Absorption involves a transition between two energy levels. In the presence of microwave energy, molecules in the lower level absorb energy and move to the upper level while, simultaneously, molecules in the upper level are stimulated to move to the lower level, and in the process they lose energy by radiation. A net absorption of microwave energy occurs because the Boltzmann distribution results in a slightly higher molecular population in the lower level.

Collisions among the molecules are constantly acting to restore the original Boltzmann distribution, while the microwave energy acts to equalize the populations of the two levels. The collision rate is directly proportional to pressure (for a fixed composition of the gas). At low pressures, the collision rate is small and a relatively small amount of microwave power will cause the populations of the two levels to approach equality. This result is power saturation. With a further increase in microwave power, the line height does not increase; the line becomes broader. As gas pressure is increased, the collision rate increases and a larger amount of microwave power is required to produce power saturation.

Molecular collisions and power saturation cause the observed microwave line to broaden with a resultant loss in line height. The collision rate increases with gas pressure and thus the line width increases with pressure. At some pressure in the range of 10 to 20 mtorr, an increase in sample pressure produces essentially no increase in line intensity--only additional line broadening.

From line width measurements, collision rates and effective collision diameters can be determined. In turn, from collision diameters information on the type of molecular interactions,

i.e., dipole-dipole, dipole-quadrupole, etc., can be evaluated. To the analyst, line width measurements are important because they allow him to estimate the usefulness of a particular quantitative procedure.

The overall effect of temperature on microwave lines is a reduction in line height with increasing temperature. If we compare identical gas samples at the same pressure but different temperatures, the higher temperature sample will have (1) a smaller population difference between a given pair of energy levels, (2) a higher collision rate, and thus a wider line, and (3) a smaller total number of gas molecules. All three effects act to decrease the observed line height. For maximum sensitivity a microwave spectrometer should be operated at the lowest possible temperature.

III. DESCRIPTION OF THE MICROWAVE SPECTROMETERS

Two spectrometers were used to obtain the experimental results of this report. Both spectrometers are equipped to operate in K-band (approximately 17,500 MHz to 27,000 MHz) and, except for equipment details, are very similar. Spectrometer no. 1 is our original spectrometer, while spectrometer no. 2 was constructed later and was designed as a more versatile instrument for analytical development work.

The gas cells are Stark cells of X-band wave guide with a metal Stark septum centered in the guide and parallel to the broad faces of the wave guide. The septum is insulated by strips of Teflon® along the two narrow sides of the wave guide. Each cell is 10 feet long. The cell for spectrometer no. 1 is brass, while the cell for spectrometer no. 2 was constructed entirely of stainless steel. In addition, the cell of spectrometer no. 2 was constructed with pumping ports sections at both ends of the cell to permit samples to be pumped through the cell in a continuous flow-through system. Cell no. 2 is designed to operate at temperatures up to 250°.

The square wave Stark modulation voltage for both spectrometers is obtained from Industrial Components Incorporated square wave generators which operate at either 100 kHz or 5 kHz and produce a peak voltage of 2000 volts. The phase lock amplifiers are the Electronics, Missiles and Communication, Inc., model RJB. The 100 and 5 kHz preamplifiers were constructed at Dow. The crystal detectors are selected type 1N26C (Sylvania) crystals mounted in Microwave Associates K-band crystal holders.

Microwave power levels were measured by means of a Hewlett Packard model 431B power meter. When microwave power leveling

was required, a leveler which was designed and constructed at Dow was used. This unit levels power by automatically adjusting the input power to the absorption cell to maintain a constant voltage across the crystal load resistor and thus, a constant microwave power level at the crystal detector.

The sample introduction system of spectrometer no. 1 is equipped for direct introduction of gases through quick-couple connectors. Both gases and liquids may be introduced through a silicon rubber septum by means of microsyringes. The sample introduction system of spectrometer no. 2 was specifically designed for optimized handling of analytical samples. It was modeled after mass spectrometer inlet systems constructed here at Dow. The entire system can operate from room temperature to 250°C. Samples can be introduced by microsyringes through a rubber septum, by direct introduction through a quick-couple connector, or solids and liquids can be placed in cups of Teflon® and loaded through a vacuum lock system. Both systems are equipped with spherical glass ballast volumes to reduce gas adsorption effects on pressure.

Diaphragm capacitance type micromanometers are used to measure sample pressures in both spectrometers. Spectrometer no. 1 is equipped with an Atlas-Werke, A.G., model EW230 micromanometer which measures pressures from 0 to 200 mTorr, while spectrometer no. 2 is equipped with an MKS Instruments, Inc., model 78M-XRP capacitance manometer with a range of 0 to 10 Torr in eight ranges which are selected by a switch.

The microwave source for spectrometer no. 1 is a modified Alfred backward wave oscillator power supply and a Varian Associates model 163 backward wave oscillator. Sweep controls were constructed at Dow. The source for spectrometer no. 2 is a Hewlett

Packard model 8690A source control with reference oscillator, synchronizer and counter for direct read-out of frequency. A Hewlett Packard model 8696A backward wave oscillator is used.

Approximate frequencies were measured with Hewlett Packard model K532A cavity-type wavemeters. More exact frequency measurements were based on harmonics generated by crystal oscillator and frequency multiplier units manufactured by the Micro-Now Instrument Co. 50 and 450 MHz signals from the frequency multiplier were mixed and applied to a harmonic generating 1N26C crystal which was mounted on a combination directional coupler and attenuator in the plumbing from the source to the cell. A parallel connection to the crystal was made to the input of a radio receiver. With the receiver tuned to 25 MHz, marker output from the receiver occurs every 50 MHz at those times when the microwave frequency of the source and a harmonic generated at the crystal differ by 25 MHz. The receiver output is applied to the "Zero Beat In" terminals of the phase lock amplifiers. With proper polarization of the connections, sharp frequency markers are produced every 50 MHz on the spectral chart and in a direction opposite to that of the absorption line. Frequencies of the markers end in -25 or -75 MHz, such as 22225, 22275, 22325 and 22375. Frequencies accurate to ± 1MHz can be obtained by linear interpolation between two frequency markers. This system is simple to use, requires no prior knowledge of line frequencies to be expected, and the accuracy is more than adequate for line identification in practical analytical applications. For more accurate frequency measurements, more elaborate (and more time-consuming) techniques are available.

IV. SPECTRA, COMMENTS, AND SENSITIVITY LIMITS FOR THE COMPOUNDS STUDIED

The compounds selected for study in this program were SO_2, NH_3, CH_2O, NO_2, CH_3SH, and Acetone. A considerable amount of data were also obtained for OCS because of its high intensity and ease of handling. These compounds cover a range of types and problems of potential interest in air pollution studies. Carbonyl sulfide has a very large absorption coefficient and is a linear molecule; thus it has a very strong and uncomplicated microwave spectrum. It is also generally used as a calibration standard.

Sulfur dioxide has a strong and relatively uncomplicated spectrum and is of interest because it is found in vent stack emissions from power plants. Methyl mercaptan has a reasonably strong microwave spectrum. It is rapidly adsorbed on the walls of an absorption cell and provides an interesting model for adsorption problem studies. Formaldehyde was chosen as a representative oxygenated compound typical of automotive exhaust emissions. Acetone is an example of a compound with less intense microwave lines but a very complicated spectrum with hundreds of absorption lines.

NO_2 was included as a compound of great interest in automobile emissions and other pollution areas. The problem in working with NO_2 is its high chemical reactivity. At the start of this project, we questioned whether meaningful measurements could be made for NO_2. Certainly the problems of reactivity and adsorption make a quantitative determination of NO_2 at low levels very unreliable.

NH_3 is of interest in any study of analytical applications of microwave spectroscopy because of its very strong absorption,

possibly the strongest microwave absorber of all molecules. In principal, the sensitivity of a microwave spectrometer for NH_3 should be the highest of all molecules. However, its strong adsorption to the cell walls of a spectrometer causes the loss of NH_3 from samples of low concentration. A trace of NH_3 in a sample can easily disappear on the cell walls. A further complication is the appearance of small amounts of NH_3 from compounds containing amine groups. Every amine type of compound, including aniline, that we have examined has shown an easily observed spectrum of NH_3. In mixtures of amines and NH_3, the source of the NH_3 would always be in doubt.

Tables I through VI give the spectral data that we have observed for OCS, SO_2, CH_2O, NO_2, CH_3SH, and a part of the spectrum of acetone. Our catalog for acetone includes 205 measured line frequencies. These are only a portion of all the lines observed in the complete spectrum. No tabulation was given for NH_3 since a rather complete listing with intensity data is given in NBS Circular 518, Molecular Microwave Spectra Tables. The observed frequencies in the tables were determined by interpolating between frequency markers separated by 50 MHz. Frequencies reported in the literature, or measured accurately here at Dow, are included in the second column to give a measure of the accuracy of the survey measurements using markers. The Dow data reported under literature frequencies is believed to be accurate to at least ±0.02 MHz.

The intensity data of Tables I through VI are all corrected to OCS as a standard, except for a difference in microwave power level. The data of the first three tables were obtained with a power level of 0.1 mw while Tables IV, V, and VI were obtained with 1.0 mw.

Table I

OCS

Power = 0.1 mw

Observed Freq. (MHz)	Literature Freq. (MHz)	Intensity (divisions)	Intensity, %
22820		6.5	0.1
23661	23660.62[2]	2.5	0.05
23731	23731.30[3]	182	4.0
23761	23760.67[4]	7.0	0.2
23785	23784.95[4]	7.3	0.2
24014		3.5	0.1
24021		19.5	0.4
24248		39	0.9
24254	24253.51[1]	58	1.3
24326	24325.92*	4550	100
24356	24355.50[1]	183	4.0
24381	24381.07[1]	183	4.0
24401		26	0.6

*Frequencies measured at Dow to an accuracy of better than ±0.02 MHz.

Table II

SO_2

Power = 0.1 mw

OCS 24326MHz line = 4550 div.

Observed Freq.(MHz)	Literature Freq.(MHz)	Intensity (divisions)	Intensity,%
17971		17	1.4
18569		4	0.4
18977		2	0.2
19096		2	0.2
19227		2	0.2
19230		6	0.5
19250		2	0.2
19306		4	0.4
19636		221	17.9
19681		17	1.4
20103		3	0.2
20261		6	0.5
20335	20335.43*	721	59
20384		6	0.5
20548		34	2.8
20701		18	1.5
20785		3	0.2
20835		1	0.1
21265		15	1.2
21762		2	0.2
21768		2	0.2
22065		77	6.2
22220	22220.32[5]	51	4.1
22482	22482.51[5]	822	67
22734	22733.83[5]	61	5.0
22904	22904.95[5]	64	5.2
22929	22928.45[5]	47	3.8

Table II

SO_2 (Continued)

Observed Freq.(MHz)	Literature Freq.(MHz)	Intensity (divisions)	Intensity,%
23035	23034.80[5]	221	18
23207		10	0.8
23415	23414.25[5]	620	50
23733	23733.03[5]	45	3.7
24040	24039.65*	853	69
24083	24083.46*	550	45
24302		4	0.3
24319		174	14.1
24796		19	1.5
24916		17	1.4
25050		430	35
25171		45	3.7
25393		1232	100
25884		11	0.9
26038		31	2.5
26412		90	7.3

*Frequency measured at Dow to better than ±0.02 MHz.

Table III

Formaldehyde

Power = 0.1 mw

OCS 24326 MHz line = 4550

Observed Freq. (MHz)	Literature Freq. (MHz)	Intensity (divisions)	Intensity, %
18841		2	0.2
19595	19595.23[6]	73	7.4
20426		1	0.1
20650		12	1.2
20735		11	1.1
20794		2	0.2
22002		5	0.5
22966	22965.57*	982	100
24068	24068.35*	831	85
24731		2	0.2
26331		2	0.3
26362	26358.82[6]	15	1.6

*Frequencies measured at Dow to an accuracy of better than ±0.02 MHz.

Table IV

NO_2

Power = 1 mw

OCS 24326 line = 4550 at 0.1 mw

Observed Freq. (MHz)	Literature Freq. (MHz)	Intensity (divisions)	Intensity, %
26563		1860	92
26569		2018	100
26577		1744	86
26604		74	3.7
26620		1669	82
26633		320	9.0
26634		1585	79
26647		1479	73
26666		74	3.7
26674		60	3.0
26777		381	19

Table V

CH_3SH

Power = 1 mw

OCS 24326 line = 4550 at 0.1 mw

Observed Freq. (MHz)	Literature Freq. (MHz)	Intensity (divisions)	Intensity, %
18041		15	2
18258		10	1
18432		40	5
18495		69	8
18779		14.6	2
18805		93	11
18824		51	6
18896		24	3
18993		20	2
19027		30	4
19115		5	1
19173		32	4
19212		5	1
19274		12	1
19334		40	5
19488		15	2
19511		49	6
19568		199	24
19703		51	6
19913		55	7
19973		7	1
20000		63	8
20051		55	7
20139		57	7
20242		74	9
20385		66	8
20645		46	6

Table V

CH_3SH (Continued)

Observed Freq. (MHz)	Literature Freq. (MHz)	Intensity (divisions)	Intensity, %
20929		52	6
21056		65	8
21107		7	1
21113		13	2
21130		55	7
21231		81	10
21519		74	9
21557		66	8
21735		70	8
21767		36	4
21865		149	18
21877		85	10
21902		72	9
21942		72	9
21974		117	14
22270		76	9
22332		97	12
22560		95	12
22663		75	9
22827		225	27
23074		56	7
23078		62	7
23230		148	18
23255		294	35
23339		47	6
23495		57	7
23522		65	8
23525		56	7

Table V

CH_3SH (Continued)

Observed Freq. (MHz)	Literature Freq. (MHz)	Intensity (divisions)	Intensity, %
23565		151	18
23618		157	19
23774		47	6
23805		95	11
23989		56	7
24068		82	10
24453		26	3
24485		44	5
24879		20	2
24989		19	2
25009		34	4
25099		16	2
25122		29	4
25127		19	2
25133		22	3
25142		44	5
25144		87	10
25155		79	9
25207		225	27
25219		216	26
25292	25291.87*	840	100
25562	25290.89*	36	4
25661		276	33
25918		27	3
25999		25	3
26076		223	27
26144		29	4
26348		34	4
26388		249	30

*Frequencies measured at Dow to an accuracy of better than ±0.02 MHz.

Table VI

Acetone

Power = 1.0 mw

OCS 24326 Line = 4550 at 0.1 mw

Observed Freq. (MHz)	Literature Freq. (MHz)	Intensity (divisions)	Intensity, %
21169		183	75
21610		209	85
21953		209	85
22586		113	46
22945		107	44
23657		245	100
23910		107	44
23962		127	52
23968		194	79
24133		104	42
24901		118	48
25522		132	54
25677		113	46
25907		192	78
26402		127	52

The last column of each table gives the relative intensity of lines as a percentage of the most intense line in the spectrum of that compound. We have found such a listing very useful for qualitative identification work.

Table VII lists the frequencies of the lines selected for the study. In all cases these were the strongest lines in the spectra. For CH_3SH three lines were selected for study, each of which represented a different problem as far as adjacent line interference is concerned. The line at 23230.3 MHz has a first order Stark effect and no interference from Stark or other absorption lines near it. The 23256.9 MHz line is the second most intense line of the spectrum and has several Stark lines adjacent to it on the high frequency side. The pair of lines at 25290.8 and 25291.8 were chosen to see how measurements on such an overlapping pair of lines could be handled. The Stark components from these lines are fairly well separated and appear on the high frequency side.

Included in Table VII is a listing of interfering compounds and the approximate frequencies (±1 MHz) of the interfering lines. This listing is from data available in our files and quite probably is not complete. In addition, the possibility of interference from Stark components of lines at some distance in frequency from the selected lines can be a serious problem in quantative work. In many cases qualitative identification can be made in spite of rather severe interference, while a quantative analysis is impossible. An examination of a large catalog of microwave spectra shows that it is essentially impossible to find lines with no possible interferences. In a practical problem, however, many compounds can be eliminated from consideration from a knowledge of the origin of the problem.

Table VII

Potential Interferences with Selected Lines

Compound	Selected Freq. (MHz)	Interference	
		Freq. (MHz)	Compound
OCS	24325.9	24324	Diethylamine
		24326	Chlorobenzene
		24326	Propargyl alcohol
		24327	Chlorine trifluoride
		24327	Vinyl bromide
SO_2	24039.5	24040	trans-2,3-Epoxybutane
		24040	1,3-Dichloropropyne
		24040	Thiourea
		24041	2-Hydroxy-2-nitro propionitrile
		24041	Chloromethyl methyl sulfide
		24041	Vinyl bromide
CH_2O	22965.71	22964	4-Methyl pyridine
		22965	1-Bromo-2-butyne
		22965	Nitroethane
		22965	Thiourea
		22966	Styrene oxide
		22966	Ethanol
		22967	Chloromethyl methyl sulfide
NO_2	26620	26218	2-Hydroxy-2-nitro propionitrile
		26219	1,1-Dichloro-2,2-difluoro propane
		26221	Cyclopentanol
		26222	α-Bromoethyl benzene
CH_3SH	25290.8	25289	1,1-Dichloro-2,2-difluoro propane
	25291.8	25289	Ethylene dichloride
		25292	2-Hydroxy-2-nitro propionitrile

Table VII

Potential Interferences with Selected Lines (Continued)

Compound	Selected Freq. (MHz)	Interference	
		Freq. (MHz)	Compound
CH_3SH	23256.9	23257	Cyclopentanone
		23258	Bromocyclopentane
		23258	Tetrahydrofuran
		23259	para Fluorobenzene
CH_3SH	23230.3	23228	Diethylamine
		23228	Benzonitrile
		23229	1-Bromo-2-butyne
		23230	para Cresol
		23230	cis Dichloroethylene
		23231	para Fluorotoluene
		23231	1-Bromo bicyclo(2,2,2)octane
		23231	2-Hydroxy-2-nitro propionitrile
		23231	Chloromethyl methyl sulfide
		23231	Ethyl bromide
NH_3	23870.1	23870	Pyrrolidine
		23870	2-Pyrrolidone
		23871	Acetic acid
		23871	1,1,2-Trichloroethane
		23871	beta Chloroethyl benzene
		23872	1-Bromo-2-butyne
		23872	Methylene chloride

Because of pressure broadening and power saturation effects on microwave lines, the sensitivity limits of a microwave spectrometer must be given for a particular system. Sensitivity for a compound of low partial pressure in a mixture with air will be quite different from the sensitivity for the same pressure of the compound in the pure state. Also, the best choices of microwave power to use for maximum sensitivity in these two situations may be quite different. For the case of the pure compound at very low pressure, power saturation will limit the amount of power that can be used. The power limitation in the compound and air mixture will in general be about one milliwatt. At approximately this power level, the crystal noise is increasing as fast as the signal increases and no improvement in signal-to-noise can be gained by increasing the power level.

Table VIII gives minimum detection limits for each of the selected compounds as determined from mixtures of the compound with nitrogen. The compounds were present in the mixture at the 1.0 mole percent level or lower for these determinations. The microwave power was 1.0 mw. The total sample pressure was 100 mTorr. A scanning rate of one megaHertz per second and a lock-in amplifier time constant of 0.3 seconds were used. The NO_2 and NH_3 data were obtained from a flow-through gas system to minimize adsorption effects. As a result the sensitivity figures for these compounds may be better than one would obtain in a batch sample system. Several samples of the CH_3SH mixture were injected into the spectrometer before a run was made, in order to reduce adsorption effects. We consider that the sensitivity figures given here are useful only as guide-lines.

Table VIII

Detection Limits in Mole Percent

SO_2	0.009
CH_2O	0.008
CH_3SH	0.04
Acetone	0.16
Ammonia	0.002
NO_2	0.08

V. QUANTITATIVE ANALYSIS BY THE OPTIMUM POWER SATURATION METHOD

A. THEORY OF THE OPTIMUM POWER SATURATION METHOD

The quantitative relationships in microwave spectroscopy appear at first examination to be more direct than for other spectroscopic techniques. The absorption of microwave power depends linearly on the absorption coefficient to a very close approximation, i.e., $\Delta I = \delta l I$, where ΔI is the absorbed power, δ is the line absorption coefficient in cm^{-1}, l is the cell length in cm, and I is the incident microwave power. Two facts complicate the problem: (1) the very small difference in the molecular populations of the two energy levels involved in an observed transition permits some degree of power saturation to occur at a relatively low power level, and (2) molecular collision broadening of absorption lines (pressure broadening) is important at typical operating pressures.

Harrington[7] has described a procedure which eliminates the problems of power saturation and pressure broadening. He derived expressions which show that with a selected amount of power saturation the intensity of microwave absorption lines depend only on the partial pressure of the absorbing gas. The effects of changes in line widths on intensity measurements are eliminated.

Crable and Wahr[8] showed that the optimum power saturation procedure depends only on the detection system of the microwave spectrometer. The crystal detector output must be proportional to the square root of the microwave intensity (or power). The desired detector response can be obtained with special bridge power balancing equipment available from the Hewlett-Packard Company. We have demonstrated experimentally that a standard

broad-banded crystal detector will also provide approximately the desired response at the relatively high powers required for optimum power saturation. The response of a crystal detector to microwave power is essentially linear at microwatt levels and approaches approximately a square root dependence at milliwatt levels.

In the application of the optimum power saturation method, the spectrometer frequency is set to the center frequency of the desired line. The microwave power level is gradually increased until the line intensity reaches a maximum value. With increased power the intensity will decrease slowly; the optimum power setting is not critical. The observed line intensity at optimum power is a measure of the number of molecules of that compound per cm^3, or the partial pressure. The actual determination of partial pressure requires an experimentally determined calibration curve.

From Crable and Wahr[8] the power required at the optimum power saturation level is

$$P_{opt.} = \frac{(\Delta\nu)^2}{B} \qquad \text{(Equation 1)}$$

where $\Delta\nu$ = half line width at half power

$B = \frac{16\,\pi^2}{3\,C\,h^2} \cdot /\mu_{ij}/^2$

C = velocity of light

h = Planck's constant

and $/\mu_{ij}/^2$ = dipole moment matrix element.

For a complete derivation of B, see reference 9. Equation 1 and the definition of B show that the power required depends directly on the square of $\Delta\nu$ and inversely on $/\mu_{ij}/^2$. The

dipole moment matrix element contains terms in the rotational quantum numbers of the levels involved in the transition and the square of the dipole moment of the molecule.

The absorption coefficient is also related to $/\mu_{ij}/^2$ since:

$$\delta_o = \frac{An}{\Delta\nu} = \text{line center absorption coefficient} \quad \text{(Equation 2)}$$

Equation 2 is correct for a measurement with no power saturation and is approximated when low microwave power is used. n is the number of absorbing molecules per cm^3 while A is defined[9] as:

$$A = \frac{8\pi^2 f \nu_o^2}{3\ ckT} \cdot /\mu_{ij}/^2 \quad \text{(Equation 3)}$$

where f = fraction of molecules in lower state of the transition

ν_o = center frequency of absorbing line

T = temperature, °K

Since the line intensity observed under low power conditions depends on $/\mu_{ij}/^2$ through A, an order of magnitude estimate of microwave power required for the optimum power saturation method can be made from observed line intensities. The most intense lines require the smallest power to produce optimum saturation. Also, narrow lines require less power to saturate than broad lines.

The independence of the optimum power saturation method on line width is based on the approximation that line width contributions come only through molecular collisions and wall collisions. For reasonable pressures this approximation is good. For low total sample pressure it is no longer valid. The complete form for the signal, S_{max}, observed at optimum power saturation[8] is:

$$S_{max} = \text{constant} \cdot n \frac{\Delta\nu_W + \Delta\nu_M}{\Delta\nu_D + \Delta\nu_S + \Delta\nu_W + \Delta\nu_M} \qquad \text{(Equation 4)}$$

where $\Delta\nu_D$ = Doppler line broadening contribution to line width

$\Delta\nu_S$ = Stark modulation contribution to line width

$\Delta\nu_W$ = Wall collision contribution to line width

$\Delta\nu_M$ = Molecular collision contribution to line width

At high pressures, both the numerator and denominator of Equation 4 are dominated by $\Delta\nu_M$. At low pressures $\Delta\nu_M$ approaches the value of the other line width contributions, and S_{max} no longer depends only on n, the partial pressure of the desired compound.

B. EXPERIMENTAL RESULTS FOR THE OPTIMUM POWER SATURATION METHOD

The OCS line at 24325.92 MHz was selected for a test of the optimum power saturation procedure because its high intensity and narrow line width make it relatively easy to power saturate. Our line width measurements gave a value of 6.25 kHz per mTorr of pressure for the molecular collision line width parameter. Figure 1 shows a plot of OCS line intensity versus OCS pressure. The data form a reasonable straight line. Note that the low pressure data deviates from a straight line as discussed above.

The data of Figure 1 did not fit all of our expectations. The line width, $\Delta\nu$, in Equation 1, is proportional to pressure at high pressures. Thus, according to Equation 1, the power required for optimum saturation should be proportional to the square of the pressure. 3.60 mw were required at a pressure of 20 mTorr and 6.26 mw at 33.5 mTorr. However, the square of the ratio of these pressures is 2.81, and that times 3.60 mw is 10.1 mw, which is considerably larger than the 6.26 mw observed. Two factors may explain this result: (1) the operating

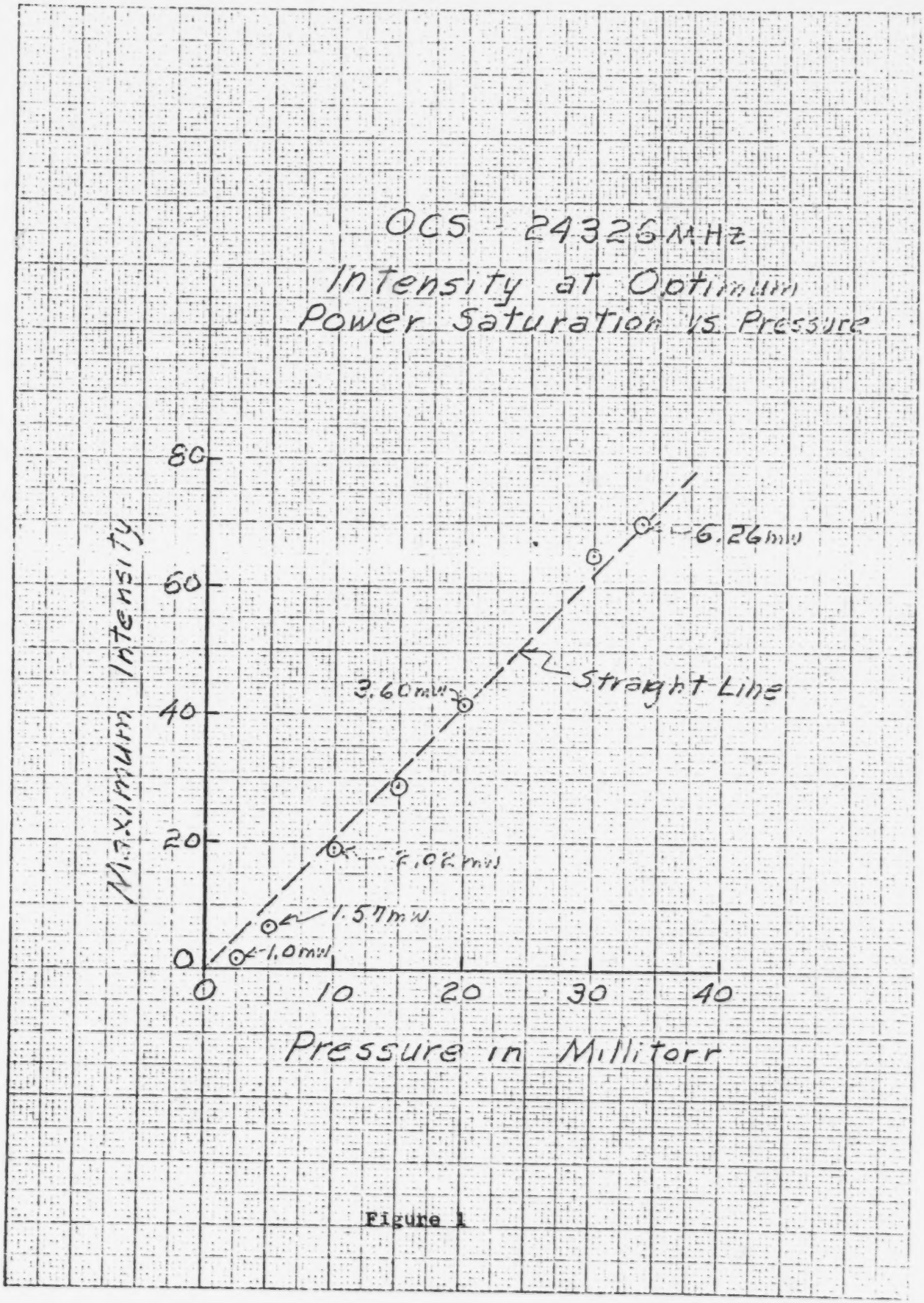
OCS - 24326 MHz
Intensity at Optimum
Power Saturation vs. Pressure
Maximum Intensity
80
60
40
20
0
6.26mw
3.60mw
Straight Line
1.57mw
1.0mw
0
10
20
30
40
Pressure in Millitorr

Figure 1

characteristics of our detector do change with power and (2) the very narrow molecular collision line width parameter makes the required approximation that the molecular collisions dominate the line width be somewhat poorer than desired. Using a Stark modulation frequency of 100 kHz the observed half line width at half power was 205 kHz at 20 mTorr of which molecular collisions contributed only 125 kHz.

Better results are obtained from Equation 1 if actual measured line widths are used. At a Stark frequency of 100 kHz our measured half line widths were 205 and 278 kHz at pressures of 20 and 33.5 mTorr, respectively. The square of the line width ratio is then 1.84 and predicts, from the 20 mTorr data, a required power of 6.6 mw at 33.5 mTorr. This is in reasonable agreement with the 6.26 mw observed.

As part of our evaluation it was necessary to have a means of estimating the microwave power required for the optimum power saturation method for a range of molecules. For this reason the following expression was derived. From Equation 2 an expression for the observed line intensity can be given as:

$$\text{Center line intensity} = C = \frac{A \cdot n}{\Delta\nu} \qquad \text{(Equation 5)}$$

$$\text{or } A = \frac{C\Delta\nu}{n}$$

The microwave power term has been left out of Equation 5. It is assumed here that the line intensities are measured at a power level of 0.1 mw to minimize power saturation effects.

From the definitions of A and B

$$B = A \cdot \frac{2kT}{h^2 f \nu_o^2} = \frac{C\Delta\nu}{n} \cdot \frac{2kT}{h^2 f \nu_o^2} \qquad \text{(Equation 6)}$$

Substituting Equation 6 in Equation 1, we obtain

$$P = \frac{(\Delta\nu)^2}{\left(\frac{C\Delta\nu}{n}\,\frac{2kT}{h^2 f\nu_o^2}\right)} = \frac{\Delta\nu \cdot nf \cdot \nu_o^2}{C} \cdot \text{constant} \qquad \text{(Equation 7)}$$

If $\Delta\nu$ is substituted for n (since $\Delta\nu$ is proportional to n) and, further, f is lumped into the constant, Equation 7 becomes:

$$P = \text{constant} \times \frac{(\Delta\nu)^2 \nu_o^2}{C} \qquad \text{(Equation 8)}$$

From the OCS data of 3.60 mw and a $\Delta\nu$ of 205 kHz, the constant is 1.12×10^{-9} and Equation 8 becomes:

$$P_{(mw)} = 1.12 \times 10^{-9} \cdot \frac{[\Delta\nu(kHz)]^2\,[\nu_o(MHz)]^2}{C} \cdot \frac{\text{OCS Ints.}}{4550}$$

(Equation 9)

The OCS Ints. is the observed line intensity in divisions of the OCS 24325 MHz line for a microwave power of 0.1 mw and a pressure high enough to be in the pressure broadened region. The last term of the equation is included for approximate standardization of different spectrometers. The $\Delta\nu$ here is the observed half line width at half power measured or calculated at the sample pressure of interest in the analysis. If the line width parameter L is known, then the line width can be calculated by multiplying L by the pressure in units compatible with L. Our experimental work showed that only for OCS with its very narrow collision broadened line width was the line width broadening from Stark modulation of significance.

In gas mixtures, the actual line width of the desired line in the mixture must be used. The OCS measurement discussed above required 3.60 mw for 20 mTorr of pure OCS. A partial pressure of 20 mTorr of OCS in a mixture at a total pressure of 100 mTorr

would require considerable more power to produce optimum power saturation. The amount of power would depend on the nature of the other components in the mixture with respect to their collision rates with OCS molecules.

Table IX gives the microwave power needed for optimum saturation of a number of typical molecules. These data were calculated from Equation 9 for a sample of the pure compound at a pressure of 20 mTorr. Although these calculated results should only be considered as good estimates, they do show that relatively high microwave powers are required even for molecules which are usually considered to be strong microwave absorbers. Since the microwave power available in a K-band spectrometer is of the order of 10 mw, and is lower yet for spectrometers operating at higher frequencies, the large power requirement places a severe limitation on the general application of the method. In the only published work of an application of this technique, Funkhouser[10] et.al.found that insufficient power was available in R-band to make measurements above 20 mTorr total pressure of a 10.1 volume percent sample of acetone in nitrogen.

The application of the optimum power saturation method to air pollution samples is somewhat more favorable. Such samples will consist of small concentrations of gases of interest in the presence of large concentrations of air. The effect on line width of collisions between the microwave absorbing molecules and nitrogen or oxygen molecules is small by comparison with the effect of collisions among the absorbing molecules themselves. Thus, the microwave power required is reasonable - of the order of a few milliwatts. Although the optimum power saturation technique is applicable to air pollution samples, we believe that simpler and easier to use techniques are more practical, particularly for this special case. These techniques are discussed in later sections.

Table IX

Microwave Power Required for Optimum Power Saturation

		Line Width Parameter (kHz/mTorr)	Line Intensity (div)	Power Required at 20 mTorr (mw)
CH_2O	22965.57 MHz	24.7	982	150
	24068.35	20.1	831	130
SO_2	20335.43	18.0	721	83
	24083.46	17.3	550	140
CHF_3	20697.73	33.3		
CH_3CF_3	20740.53	49.8	275	90
CH_3COCH_3	21169.95	52.1	183	300
	23656.28	50.4	245	260

C. SUMMARY AND CONCLUSIONS ON THE OPTIMUM POWER SATURATION METHOD

The optimum power saturation technique allows line intensities to be used as a linear quantitative measure of concentration, or partial pressure. The line intensities at optimum power saturation are independent (at sufficiently high total gas pressures) of all line broadening effects. A calibration curve is required for each compound to be determined.

Disadvantages are: (1) high microwave powers are required and (2) each measurement requires a separate optimization of the microwave power. The high microwave power requirement eliminates the application of this technique to many molecules, if not most.

For general applications of microwave spectroscopy to quantitative determinations, other techniques, which follow, appear more attractive.

VI. QUANTITATIVE ANALYSIS BY LINE AREA MEASUREMENTS AND LINE HEIGHT MEASUREMENTS

A. DISCUSSION OF QUANTITATIVE ANALYSIS BY AREA MEASUREMENTS

A second method of quantitative analysis uses microwave absorption line areas as a measure of partial pressures of a compound. Townes and Schawlow[9] derived the following expression for microwave absorption coefficients.

$$\delta = \frac{8\pi^2 nf}{3\ ckT} /\mu_{ij}/^2 \nu^2 \cdot \frac{\Delta\nu}{(\nu-\nu_o)^2 + (\Delta\nu)^2} \qquad \text{(Equation 10)}$$

where ν = microwave frequency and ν_o = line center frequency. All other terms were defined earlier. They[9] showed that after integration over frequency, Equation 10 became:

$$\int \delta d\nu = \frac{8\pi^3 nf}{3\ ckT} /\mu_{ij}/^2 \cdot \nu_o^2 \qquad \text{(Equation 11)}$$

$$= \text{constant x n}$$

The constant of Equation 11 applies to a specific molecular absorption line and temperature. Since the observed line intensity is microwave power, I, times δ, the integrated observed line area is:

$$\text{Integrated line area} = \text{constant x I x n} \qquad \text{(Equation 12)}$$

Thus for a fixed power level the absorption line area is linearly proportional to the partial pressure. It is assumed that the power level is low enough to minimize power saturation effects. For molecules other than very strong absorbers this condition is easily satisfied.

An examination of Equation 10 suggests a simpler method of analysis without requiring the direct measurement of line areas. When Equation 10 is written for the line center frequency, it becomes:

$$\delta = \frac{8\pi^2 nf}{3\,ckT} /\mu_{ij}/^2 \nu_o^2 \cdot \frac{1}{\Delta\nu} \qquad \text{(Equation 13)}$$

If Equation 13 is multiplied by the line width, $\Delta\nu$, it then becomes independent of line width, or:

$$\text{Center line intensity} \times \Delta\nu = \text{constant} \times I \times n \qquad \text{(Equation 14)}$$

Equations 12 and 14 show that partial pressures can be determined from either a measurement of line area or the product of the line intensity and the half line width at half power. The line area measurements are somewhat cumbersome since it is not practical to integrate the entire frequency range experimentally. Line width and intensity measurements can be measured with reasonable ease if the frequency scanning speed and chart paper speeds of the spectrometer are selected to give a line width of 10 to 15 cm on the chart.

B. QUANTITATIVE ANALYSIS FROM LINE HEIGHT MEASUREMENTS

For certain special cases, quantitative results based on a simple intensity measurement are valid. Such cases occur when a minor component is to be determined in a mixture in which the major part of the mixture remains relatively unchanged in concentration and composition. Air pollutants will in general satisfy this requirement. For example, the line width of a small percentage of SO_2 in air is determined primarily by collisions between SO_2 molecules and oxygen and nitrogen molecules

in the air. Over the concentration range of 0 to about 5 mole percent SO_2, the SO_2 line width will be essentially a constant. Thus, the line intensity becomes a direct measure of mole percent SO_2 at low concentrations in air.

Another interesting and practical characteristic of this special case is the fact that for a given minor component concentration, the observed line intensity is independent of the total pressure. An increase in total pressure produces an increase in number of absorbing molecules per cm^3 (the minor component) which causes a proportionate increase in line area. In addition, the proportionate increase in the number of major component molecules results in an increased collision rate with the absorbing molecules and a proportionate increase in line width. The net result is a line with increased area and line width, but a line with an unchanged intensity.

C. EXPERIMENTAL RESULTS

Figure 2 is a plot of line height (Intensity) and area measurements for the OCS 24325.9 MHz line. The line intensity plot shows good linearity to 10 mTorr and reasonable linearity to approximately 20 mTorr. The straight line drawn through the area points shows that a good linear dependence exists between line area and partial pressure of OCS.

The line height and product of line height and width for the SO_2 24039.6 MHz line are shown in Figure 3. The line height curve shows reasonable linearity at pressures below 10 mTorr. The product of height and width show good linearity.

Data for CH_2O are given in Figure 4. The line height is again reasonably linear below a pressure of 10 mTorr. The plot of the

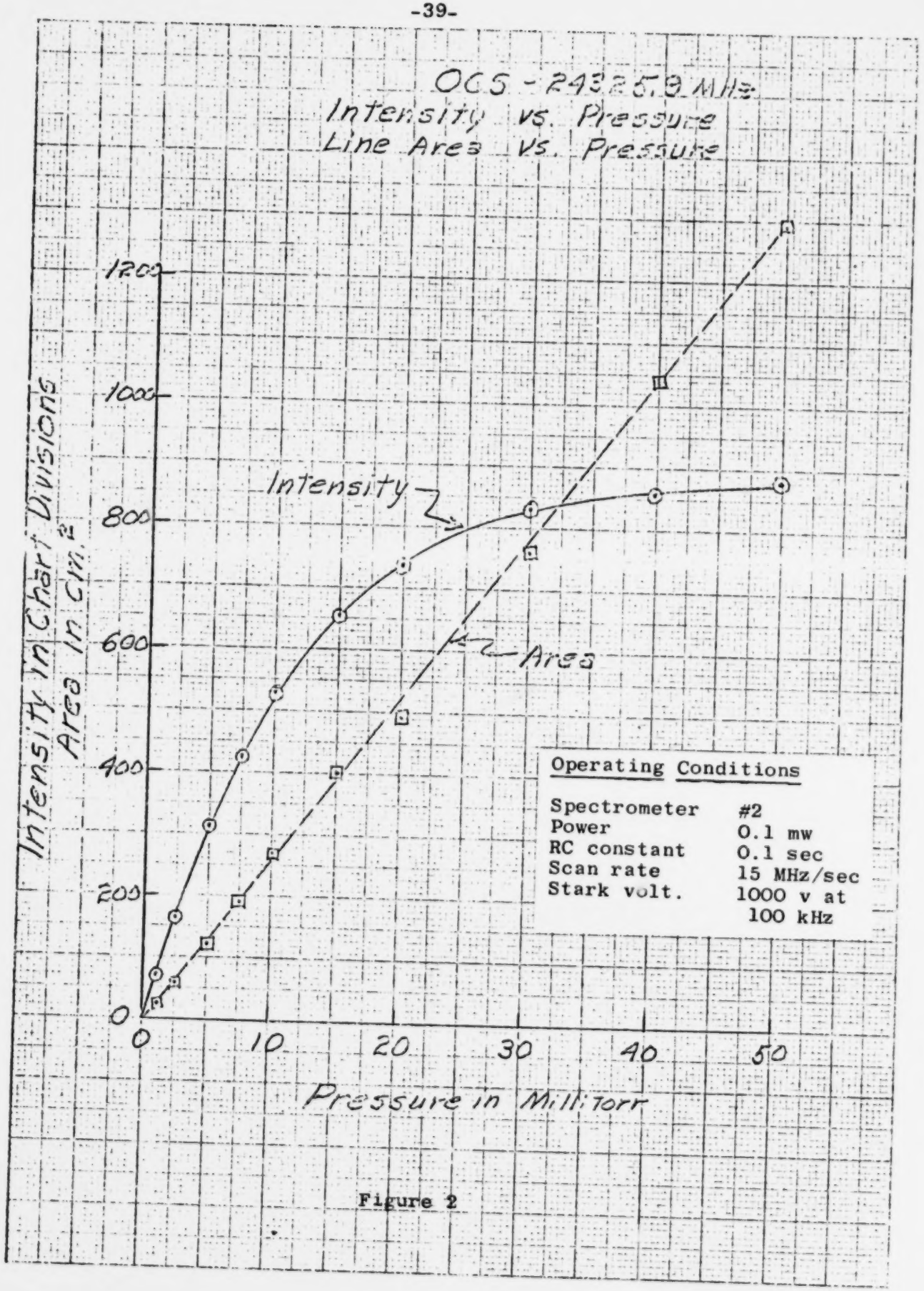
OCS - 24325.9 MHz
Intensity vs. Pressure
Line Area vs. Pressure
Intensity in Chart Divisions
Area in Cm.²
1200
1000
800
600
400
200
0
Intensity
Area
0
10
20
30
40
50
Pressure in Millitorr
Operating Conditions
Spectrometer #2
Power 0.1 mw
RC constant 0.1 sec
Scan rate 15 MHz/sec
Stark volt. 1000 v at 100 kHz

Figure 2

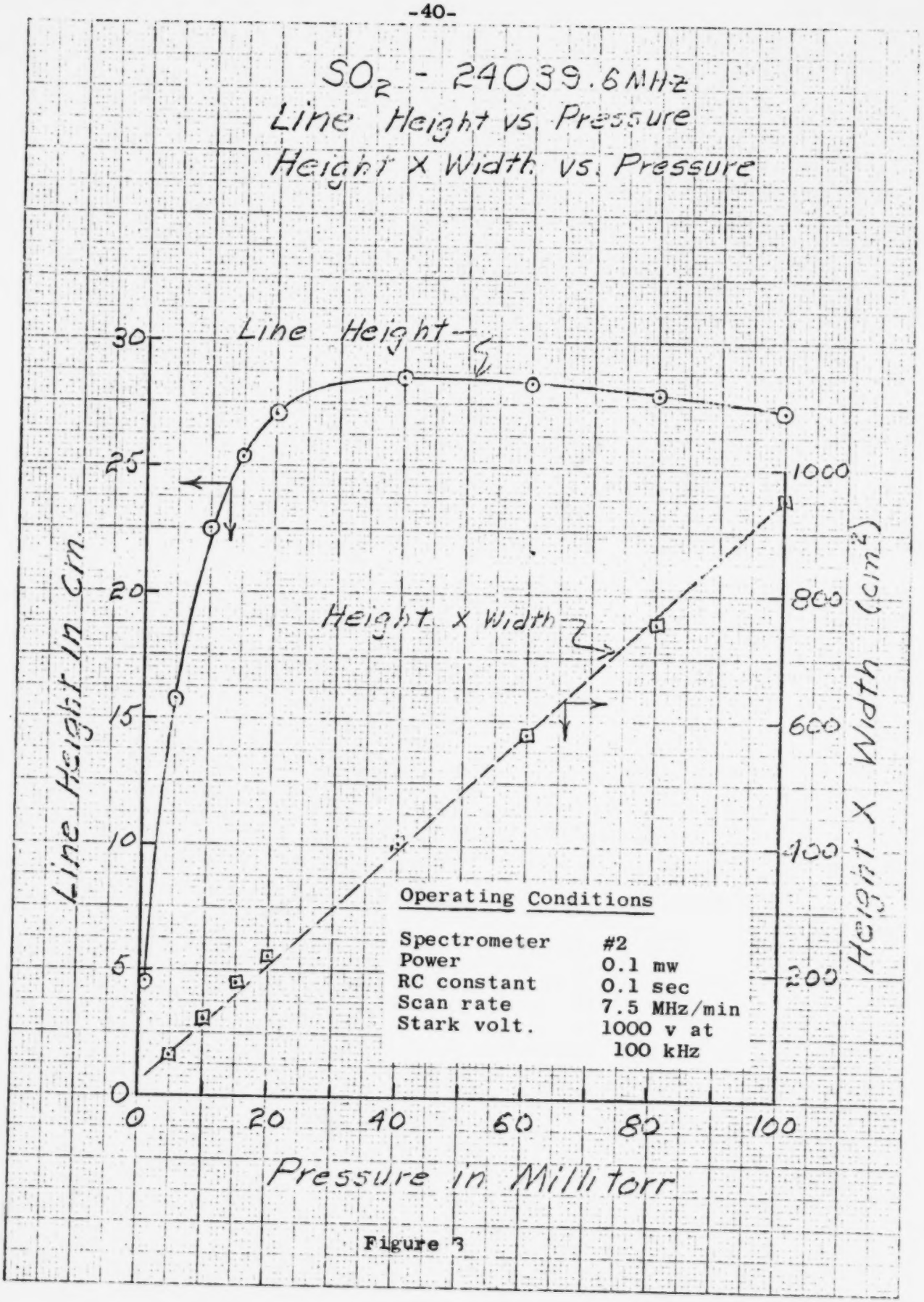
SO_2 - 24039.6 MHz
Line Height vs. Pressure
Height x Width vs. Pressure
Line Height
Height x Width
Line Height in cm.
Height x Width (cm²)
Pressure in Millitorr
0
5
10
15
20
25
30
100
200
400
600
800
1000
0
20
40
60
80
100
Operating Conditions
Spectrometer #2
Power 0.1 mw
RC constant 0.1 sec
Scan rate 7.5 MHz/min
Stark volt. 1000 v at 100 kHz

Figure 3

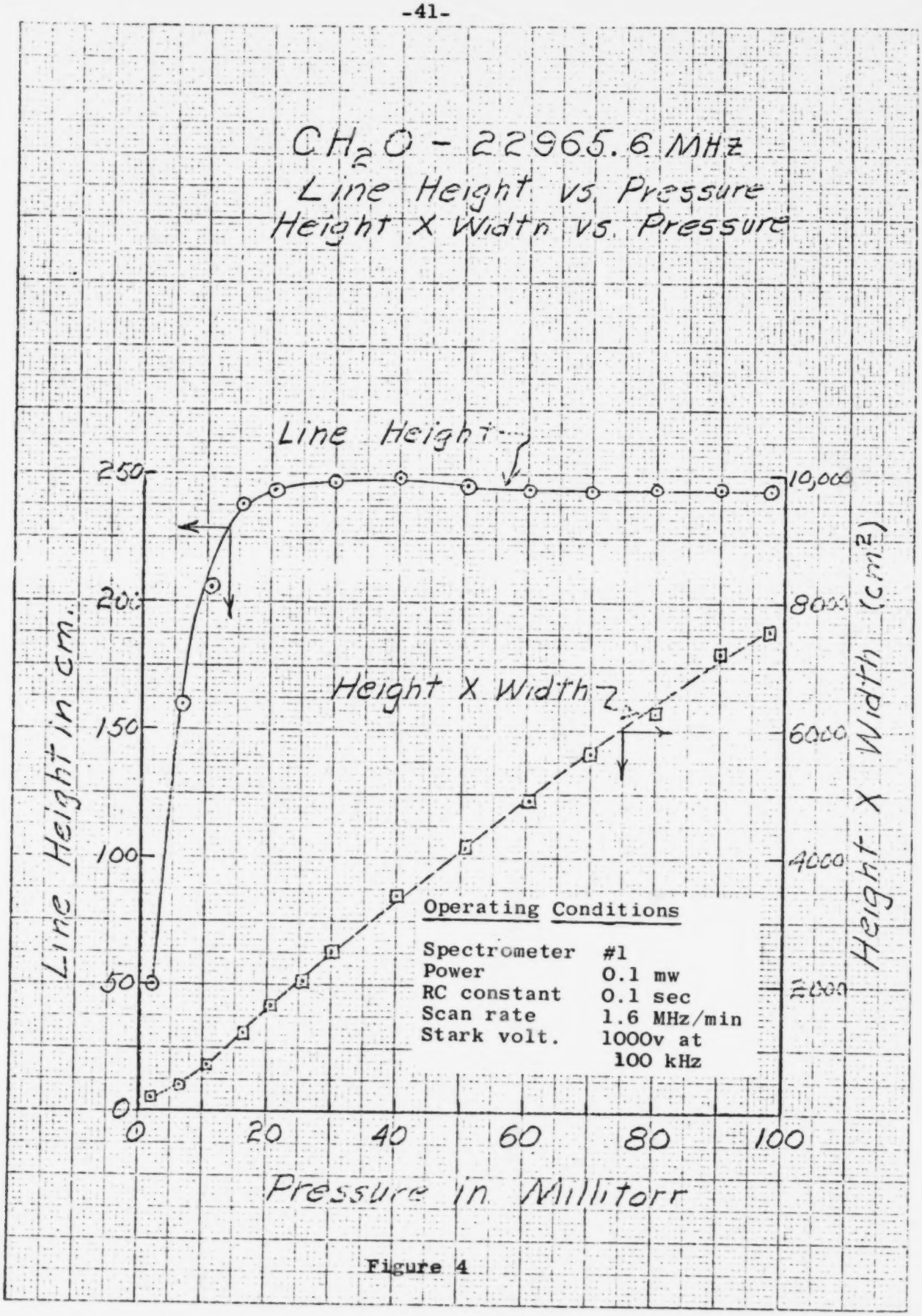
CH_2O - 22965.6 MHz
Line Height vs. Pressure
Height X Width vs. Pressure
Line Height
Height X Width^2
Line Height in cm.
Height X Width (cm^2)
250
200
150
100
50
0
10,000
8000
6000
4000
2000
0
20
40
60
80
100
Pressure in Millitorr
Operating Conditions
Spectrometer #1
Power 0.1 mw
RC constant 0.1 sec
Scan rate 1.6 MHz/min
Stark volt. 1000v at 100 kHz

Figure 4

product of height and width is a good straight line from about 10 to 90 mTorr. The low pressure end shows a slight curvature and did not appear to extrapolate to zero for zero pressure. The high pressure end (additional higher pressure points were not plotted here) shows a downward curvature toward the pressure axis. This probably results from overlap of the absorption line and Stark lines. At high pressures the Stark components for most of the compounds studied were broad enough to overlap the absorption line with a resulting decrease in line intensity.

Figure 5 gives plots of line heights and height x width products versus pressure for the acetone 21169.2 MHz line. The line height is linear at pressures below 15 mTorr. The product of height x width shows considerable scatter even though the points plotted are the average of several determinations. Some of the variation results from measurement problems because of lowered signal-to-noise for acetone. Another source of variation is the possibility of Stark component overlap from nearby lines.

Line height data for the three CH_3SH lines at 25291, 23256.9, and 23230.3 MHz are shown in Figure 6. Line heights for the doublet at the nominal frequency of 25291 were measured as the intensity of either line at low pressures where they are completely resolved. At higher pressures the highest peak, or the combined peak, was measured. The plot for the 23256.9 MHz line is quite normal with a linear portion below 10 mTorr. The plot of the 23230.3 MHz line does not appear to have a really linear portion at low pressures. The plot of the 25291 doublet has a linear portion below approximately 10 mTorr. Above 10 mTorr the general shape of the curve is quite different from the usual line height plot. The explanation is the combining of the two doublet components to form a single central peak at higher pressures.

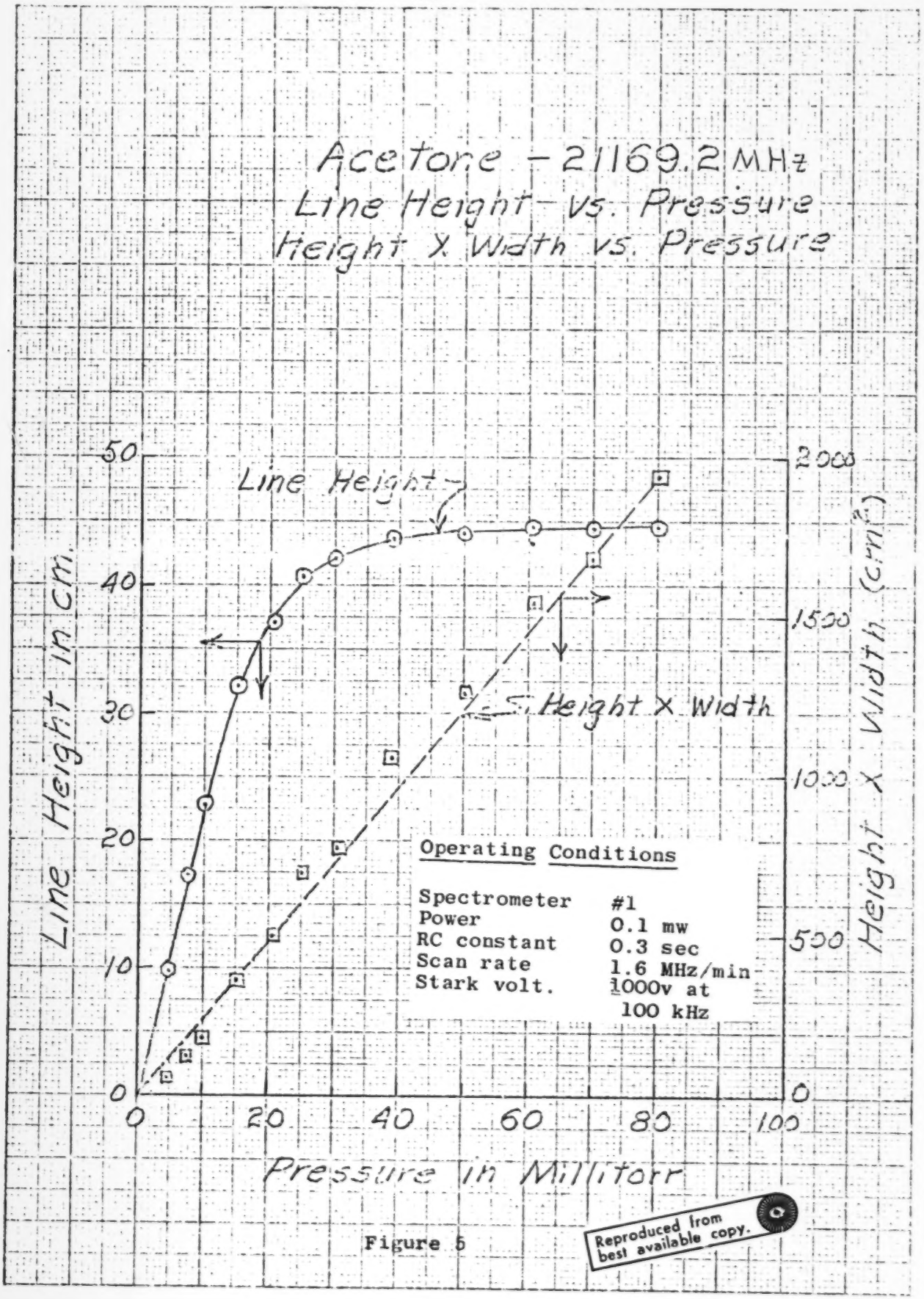

Figure 5

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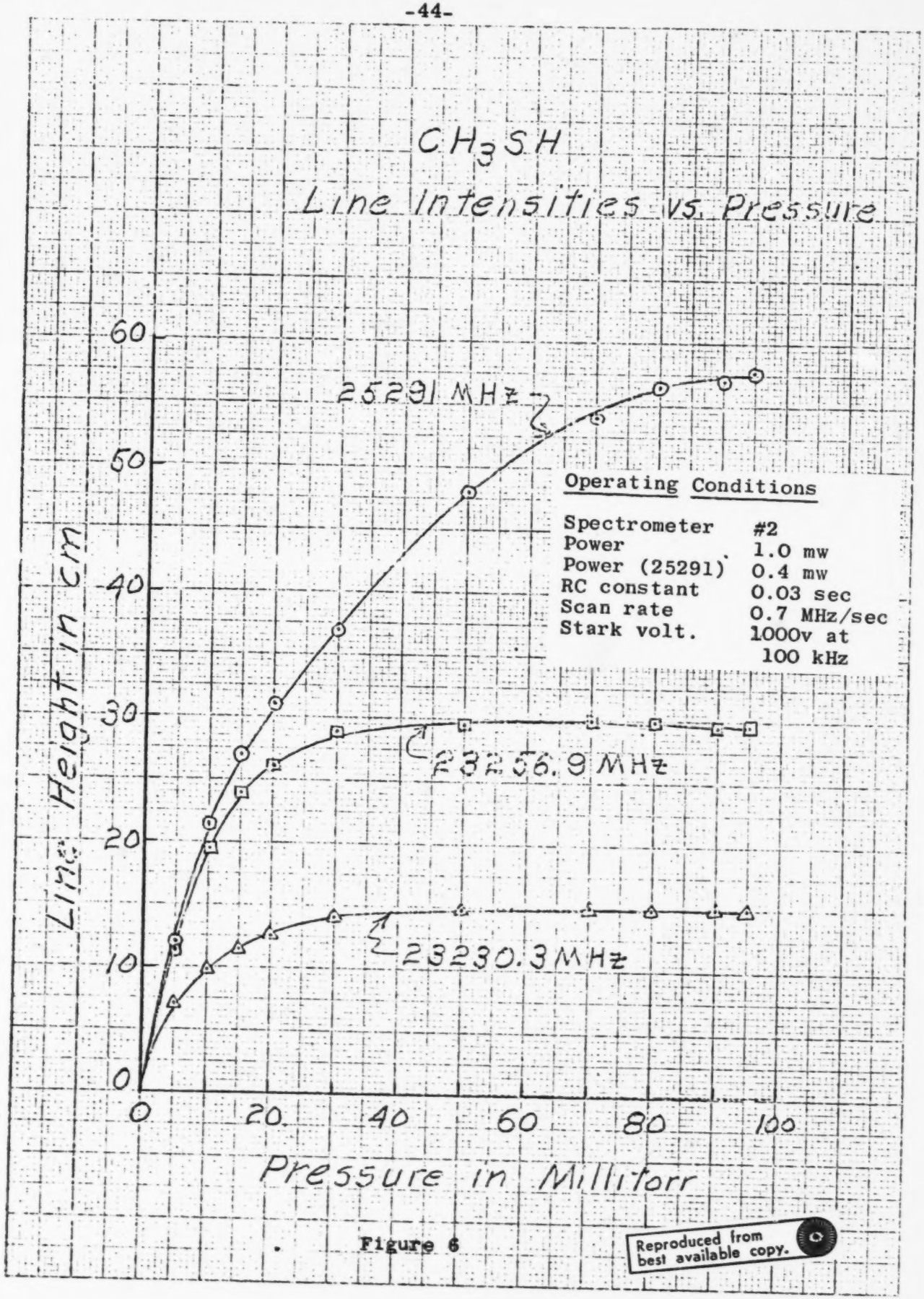

Figure 6

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Figure 7 shows the dependence of the products of height and width on pressure for the three CH_3SH lines. The plots for the 23256.9 and 23230.3 MHz lines are linear with pressure. The plot for the 25291 MHz line has a good linear portion over a pressure range of 10 to 80 mTorr. The line width used for the 25291 line was the entire width of the doublet, i.e., from the lower side of the low frequency component to the higher side of the high frequency component. The inflections in this plot are certainly a result of the method of measuring line width.

The overall result obtained from these data is that area or the product of line height and width is a linear function of pressure. The line height is linearly related to pressure at low pressures. The data for the 25291 MHz doublet of CH_3SH also approximates these relationships.

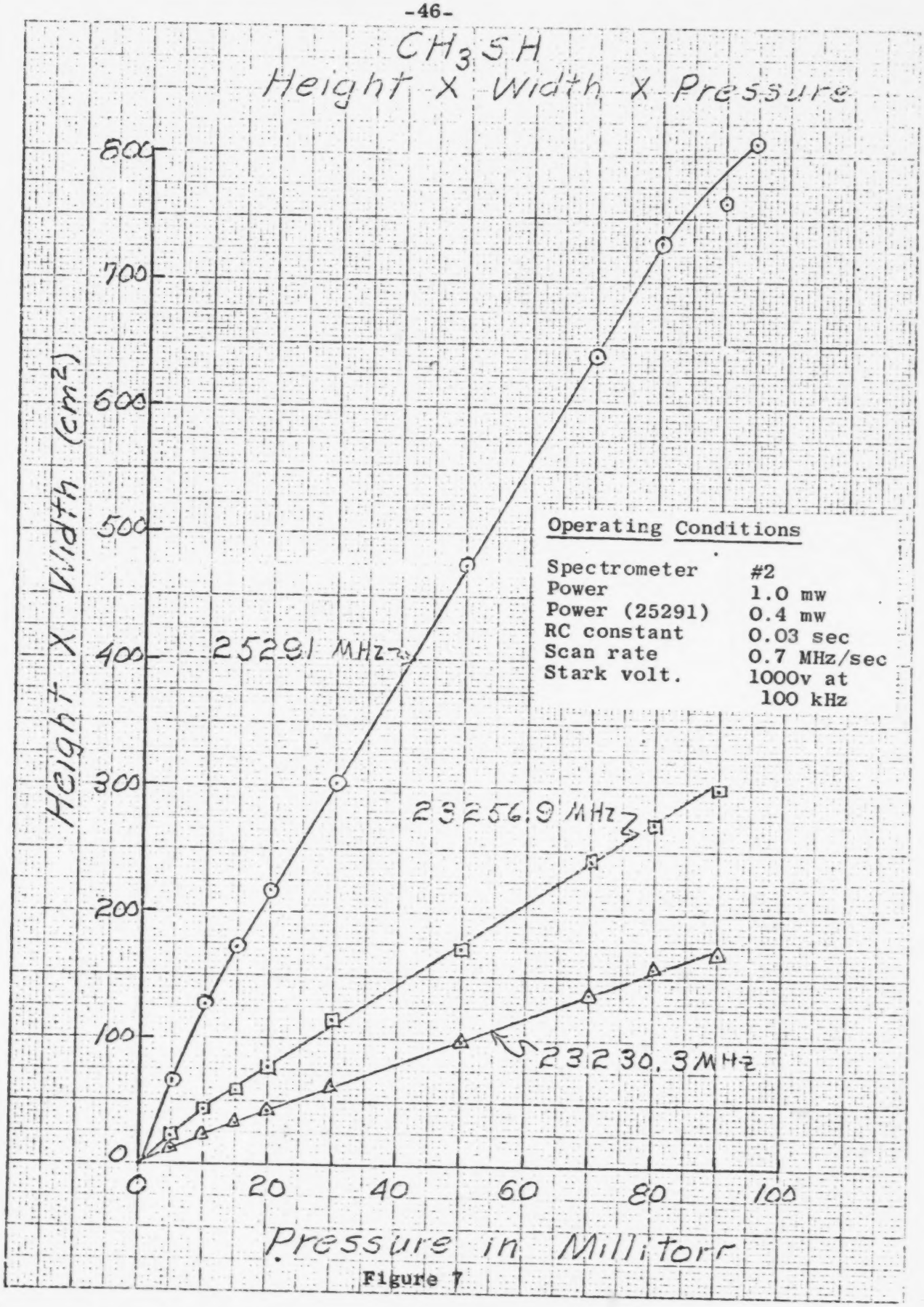
CH_3SH
Height X Width X Pressure
Height X Width (cm²)
800
700
600
500
400
300
200
100
0
25291 MHz
23256.9 MHz
23230.3 MHz
Operating Conditions
Spectrometer #2
Power 1.0 mw
Power (25291) 0.4 mw
RC constant 0.03 sec
Scan rate 0.7 MHz/sec
Stark volt. 1000v at 100 kHz
0
20
40
60
80
100
Pressure in Millitorr

Figure 7

VII. GAS BLENDS AND THE ADSORPTION PROBLEM

A gas blending system was constructed of glass and greaseless stopcocks. Gas volumes were measured in a calibrated buret at atmospheric pressure. Measured gas volumes were passed into a large mixing chamber by mercury leveling bulbs. After the gases were in the mixing chamber, a metal mixer in the chamber was raised by an external magnet and allowed to drop through the gas mixture. A spring at the bottom of the mixer cushioned the fall of the mixer at the bottom of the chamber.

The blending system and the blending technique were checked by preparing three blends of argon in nitrogen and then determining the actual concentrations with a CEC 21-104 mass spectrometer. Argon and nitrogen were used in this test to eliminate all adsorption problems. The results obtained are given in Table X below.

Table X

Argon in Nitrogen Blends

Blended Composition mole %	Mass Spectrometer Analysis mole %	Error, %
0.102	0.105	3
1.02	1.02	0
10.01	10.14	0.3

These results show that accurate blends can be prepared with this gas blending system.

Three blends of SO_2 in nitrogen were carefully prepared on the gas blending system. The blended compositions along with mass

spectrometer analyses of these mixtures are given in Table XI. Mass spectrometer analysis no. 1 was performed within two hours of the blend preparation, while mass spectrometer analysis no. 2 was run on the following day. Although the blended samples were stored in glass Shepard traps with greaseless valves, the mass spectrometer results indicate that SO_2 was being adsorbed on the walls of the container as a function of time. Included in Table XI are line heights observed for the SO_2 25392 MHz line from the three SO_2 blends. A total sample pressure of 100 mTorr and a power of 0.1 mw were used. The ratios of these line heights are in relatively good agreement with the blended composition. If the 10.0 mole % blend is taken as a standard, then percentages calculated for the other two blends based on a linear dependence of height on partial pressure are 0.97 and 0.083. A comparison of the mass spectrometer and microwave spectrometer results suggest that some SO_2 was lost from the samples through adsorption on container walls, and that possibly adsorption in the inlet of the mass spectrometer is more severe than adsorption in the microwave spectrometer. The overall result is a demonstration of the problems of preparing accurate gas blends of gases which adsorb. SO_2 is one of the easier compounds to handle in a microwave spectrometer with respect to adsorption.

Table XI

Blends of SO_2 in Nitrogen

Blended Composition mole %	Mass Spectrometer Analysis #1 mole %	Mass Spectrometer Analysis #2 mole %	SO_2 25329 MHz Height (in.)
0.100	0.052	0.023	0.47
1.00	0.76	0.68	5.48
10.01	9.82	9.33	56.4

Table XII gives information on adsorption problems as related to repeated sample introductions. Four successive introductions of the 0.1 mole % blend of SO_2 into the spectrometer caused the line height to increase from 0.37 in. to 0.50 in. A 10.0 mole % SO_2 blend was then introduced, scanned, and pumped out. The next introduction of the 0.1 mole % SO_2 blend gave a line height of 1.7 in., or 3.4 times as high as the last run before introducing the 10.0 mole % blend. The high value, of course, results from desorbing of SO_2 which had been adsorbed from the 10.0 mole % blend. These data show that the results obtained on a microwave spectrometer are highly dependent on the previous history of the spectrometer cell. This problem could be overcome by having a number of absorption cells available and arranged so that the unused cells were pumped constantly to remove adsorbed gases.

Table XII

SO_2 in Nitrogen

Total Pressure = 100 mTorr
Power = 0.1 mw

Sample mole %	Run No.	Time, min	Line Intensity, in.
0.10	1	0	0.37
0.10	2	9	0.45
0.10	3	18	0.48
0.10	4	32	0.50
10.0	5	45	60.7
0.10	6	58	1.7

Similar experiments were carried out with CH_3SH and with similar results. The cell became conditioned for CH_3SH for some days after it had been exposed to CH_3SH for an hour. After a high

pressure exposure to CH_3SH, small concentrations of CH_3SH could not be determined with accuracy. Nitrogen was introduced into the spectrometer and the cell shut off from the inlet system. After five minutes a scan for CH_3SH showed a small line from CH_3SH desorbed from the walls.

Figures 8 and 9 show the decrease in CH_3SH line height as a function of time from experiments with spectrometers no. 1 and no. 2. Each spectrometer was relatively clean of CH_3SH since the compound had not been in the spectrometers for several weeks prior to these runs. On a percentage basis, the adsorption in the brass cell of spectrometer no. 1 was worse than the stainless steel cell of spectrometer no. 2. However, these limited data should not be interpreted as a claim for a stainless steel cell as a means of reducing adsorption. Earlier experiments of ours with methyl alcohol indicated that the stainless steel cell adsorbed more rapidly than the brass cell. The CH_3SH data for spectrometer no. 2 was obtained at a higher pressure than that of spectrometer no. 1. Thus, the number of CH_3SH molecules adsorbed in the stainless steel cell was higher. Once the cell walls become conditioned, the rate of adsorption is reduced.

The work reported above in this section illustrate a major problem in the determination of concentrations of gases in small concentrations in a mixture. To handle such samples a technique for the elimination of the effects of adsorption must be devised. One such attempt, the use of a flow-through cell, is reported in the next section.

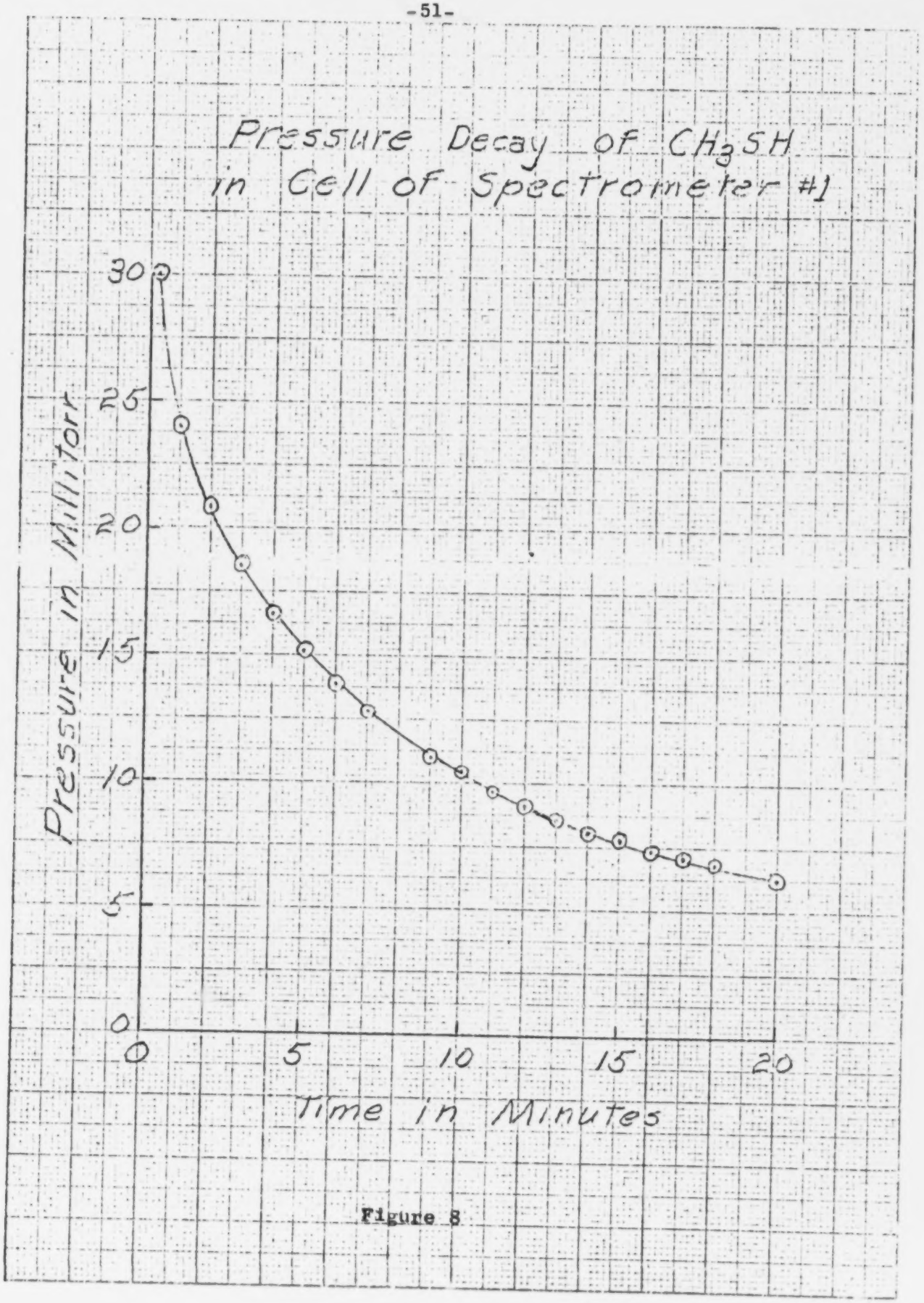
Pressure Decay of CH_3SH
in Cell of Spectrometer #1
Pressure in Millitorr
30
25
20
15
10
5
0
0
5
10
15
20
Time in Minutes

Figure 8

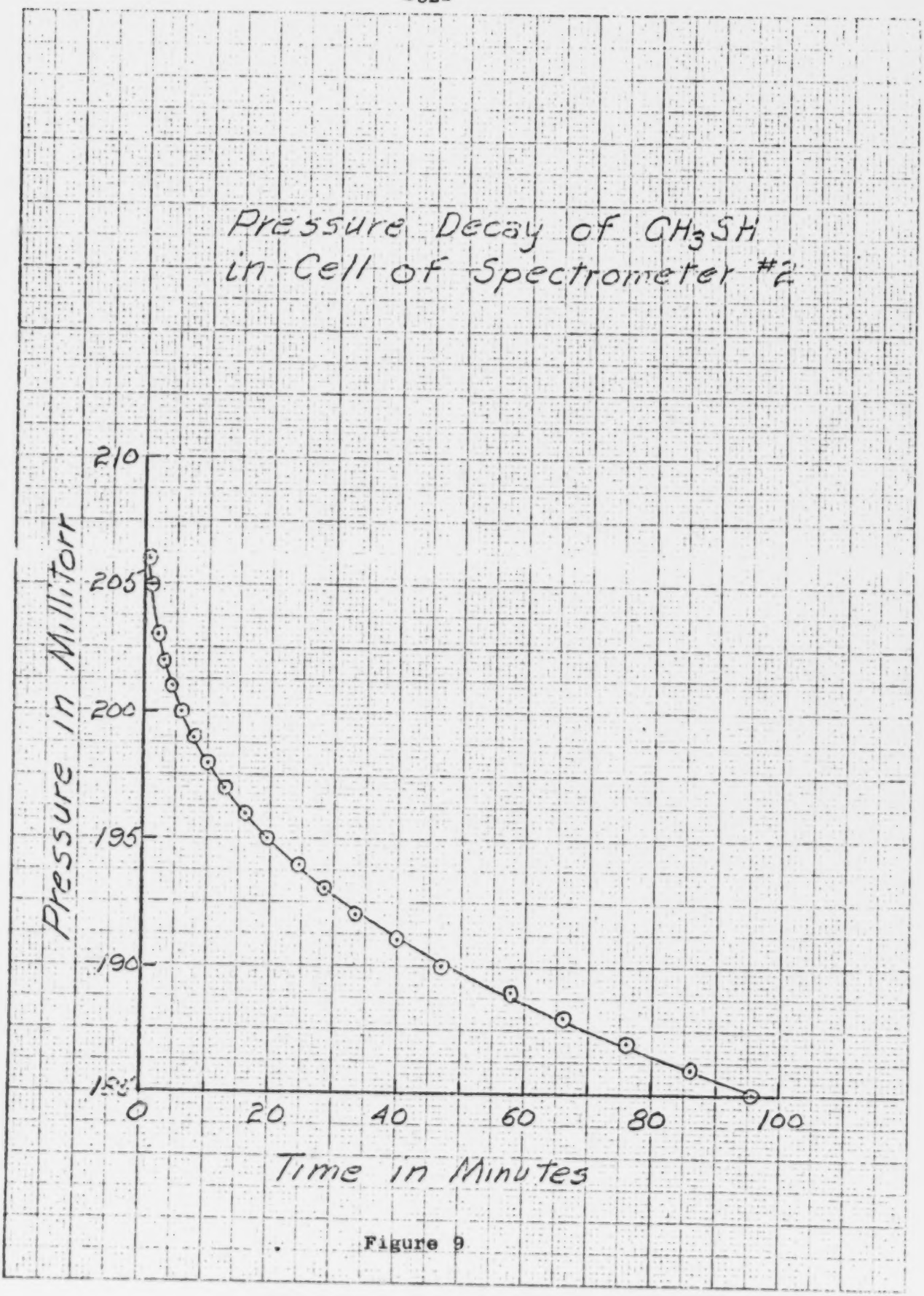
Pressure Decay of CH_3SH
in Cell of Spectrometer #2
Pressure in Millitorr
210
205
200
195
190
0
20
40
60
80
100
Time in Minutes

Figure 9

VIII. MEASUREMENTS WITH A FLOW-THROUGH CELL

A. DESCRIPTION OF THE EQUIPMENT AND PROCEDURE

Possibly the most difficult problem to overcome in the analysis of low concentrations of a gas in a mixture is the adsorption of the gas in the walls of the cell. A Stark cell of reasonable sensitivity usually has a cell 10 feet in length. The surface of the cell walls and the surface of the metal septum down the center of the cell constitute a large area for adsorption. In an attempt to overcome this problem the following experiments were carried out on a flow-through gas cell.

The stainless steel cell of spectrometer no. 2 was originally designed with pump-out ports at both ends of the cell. By attaching a vacuum system to the end of the cell away from the inlet system, a flow-through system was obtained. The vacuum system consisted of the combination of a cold trap, oil diffusion pump, and a fore pump. The vacuum system was connected to the cell through a valve and a leak. The leak which was finally chosen was a metal plate drilled with a no. 80 drill, i.e., a 0.0135 inch diameter hole. With this leak in place, the flow out of the cell is 233 mTorr cm^3/sec.

The first system for continuous mixing of gases used gas burets to determine gas flow rates and thus determine the proper settings of a pair of needle valves. This system was used in attempts to mix small amounts of SO_2 with nitrogen. Difficulties with the burets, and in maintaining the valves at a fixed position for the very low SO_2 flows caused us to discard this system.

The second system used rotameters to set the flow rates of the two gases. With a mixture flow rate of greater than 500 cm^3/min,

the smallest SO_2 rate required was several cm^3/min. This rate could be monitored with the rotameter, and the Nypro valve used did not change its setting with time. In this system, the nitrogen and SO_2, or other gas, were each passed through a valve and rotameter. The outputs from the two rotameters were joined by a Y connection and the gas mixture brought to the spectrometer introduction system through approximately 30 feet of 1/4 inch plastic tubing. A tee connection at the spectrometer with one leg open to the atmosphere and the other leg connected to the spectrometer through a valve, provided for sampling at constant atmospheric pressure. The gases exhausted from the tee were returned to the hood by means of a blower and a 4 inch exhaust line.

Pressure in the 5 liter reservoir of the sample introduction system was maintained at one Torr by properly setting the leak valve between the reservoir and the cell. A by-pass valve around the leak valve was opened initially to bring the cell pressure up to 100 mTorr quickly. Once the cell was pressurized and the flow-through system adjusted, the pressure in the cell was quite stable.

B. EXPERIMENTAL RESULTS WITH THE FLOW-THROUGH SYSTEM

Gas concentrations were based on the readings of the calibrated rotameters. A point of experimental interest was the time required to equilibrate the system. The time required for a sample to pass through the plastic connecting tube was found to be 10 to 12 seconds. Measurements made with SO_2 and nitrogen mixtures are given in Table XIII. Line heights in chart divisions for the 22482.5 MHz line, and the time required for the line height to reach a maximum after each change in SO_2 concentration are given. The times given are good to about one minute. These data show that for this particular system, about 15 minutes is required to reach equilibrium.

Table XIII

Height of SO_2 22482.5 MHz Line and Time to Reach Maximum Amplitude

Mole % SO_2	Line Height (Chart Divisions)	Time (minutes)
0.037	8.5	not measured
0.087	12.5	~5.5
0.15	17.0	6.5
0.304	28.0	10
0.622	53.5	12
1.05	89.5	~10
2.45	191	12
4.98	327	9
9.90	555	10

Figure 10 is a plot of the line height data of Table XIII. Again, these results show that for low gas concentrations an essentially linear relationship exists between line height and SO_2 concentration. The direct line height versus concentration procedure is not only the easiest technique to use, but it also does not have non-linearity problems at the low concentration range common to the other procedures.

Data from the flow-through system for CH_3SH in nitrogen are shown in Figure 11. These results for the 25291 MHz doublet are not as linear as one would like. The problem here is probably a result of overlap of the two lines with increasing pressure. From these experiments, we estimated that the least detectable concentration was 0.05 mole percent at a power of 0.1 mw in the stainless steel flow-through system.

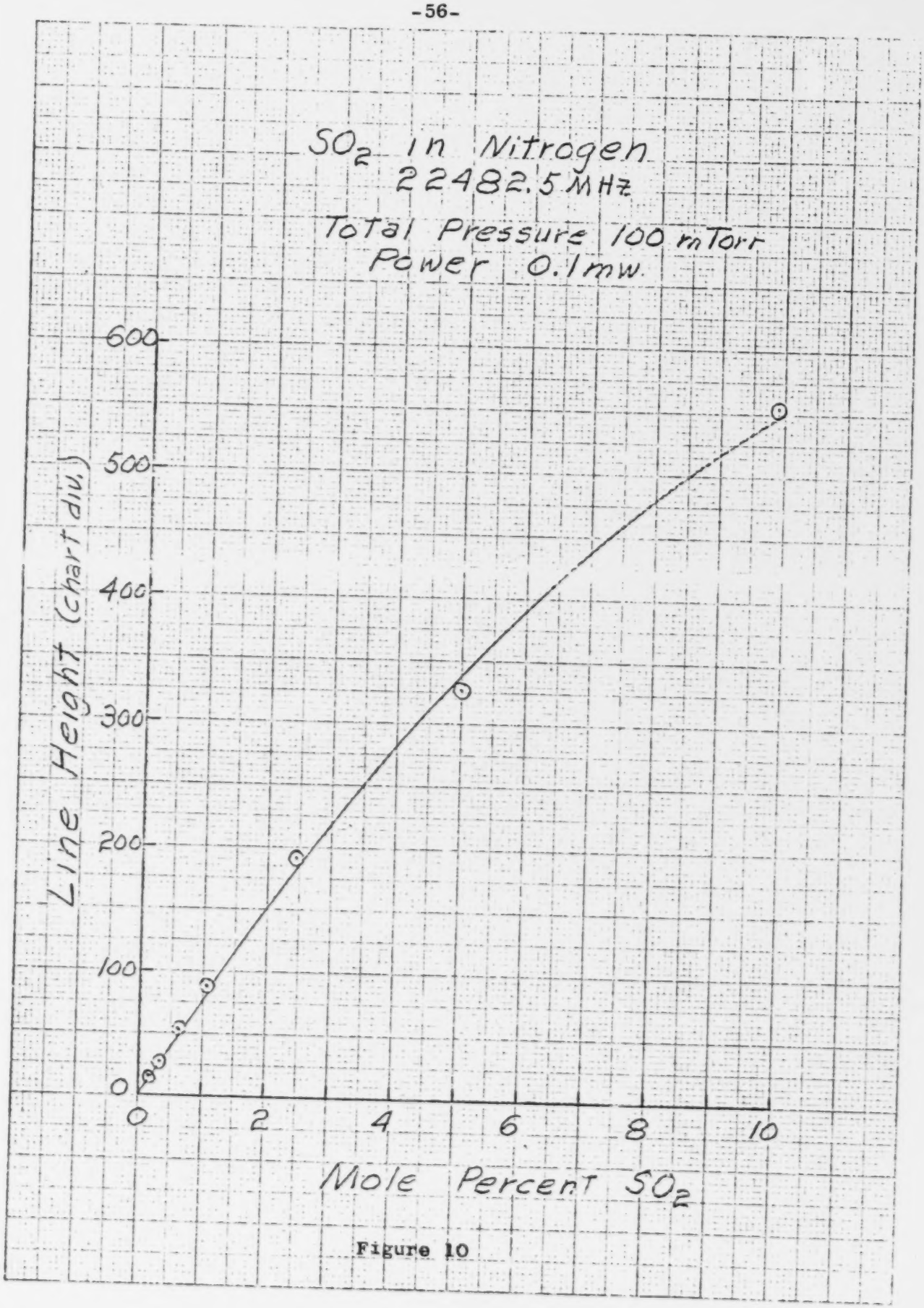
SO_2 in Nitrogen
22482.5 MHz
Total Pressure 100 mTorr
Power 0.1 mw
Line Height (chart div.)
600
500
400
300
200
100
0
0
2
4
6
8
10
Mole Percent SO_2

Figure 10

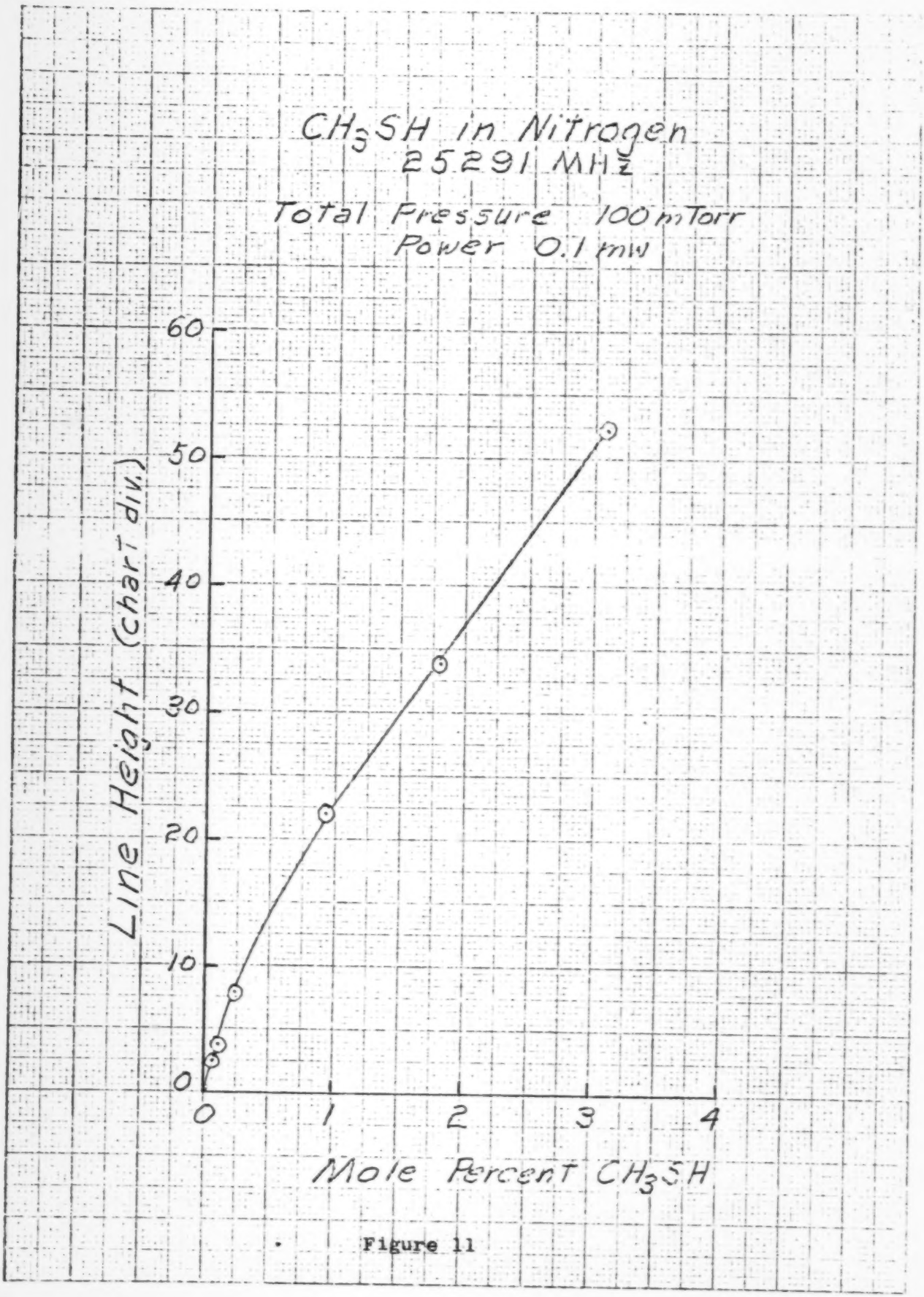
CH_3SH in Nitrogen
25291 MHz
Total Pressure 100 mTorr
Power 0.1 mw
Line Height (chart div.)
60
50
40
30
20
10
0
0
1
2
3
4
Mole Percent CH_3SH

Figure 11

Acetone in nitrogen mixtures were prepared by first passing nitrogen slowly through liquid acetone to provide a saturated acetone in nitrogen stream. This mixture was then further diluted with additional nitrogen. Acetone concentrations were based on vapor pressure data as a function of the temperature of the acetone. Data for the 21170 MHz line of acetone at a power of 0.1 mw is shown in Figure 12. The low intensity of the acetone line results in some scatter of these data. An indication of the approximate noise level is given. A reasonable straight line plot was obtained. From measurements over a range of operating conditions, we estimated that a concentration of 0.05 mole percent of acetone in nitrogen can be detected at a power level of 3 mw with this system.

The problem of producing gas mixtures of formaldehyde and nitrogen was a challenge since formaldehyde does not normally exist as a gas at higher pressures. The formaldehyde was produced by gently heating paraformaldehyde in a small furnace through which nitrogen was passed. The concentration of formaldehyde was determined from the weight loss of paraformaldehyde per unit of time and the measured flow rate of nitrogen. Although we observed no direct evidence that we later lost formaldehyde through polymerization, our calculated concentrations may be in error on the high side if polymerization did take place. Figure 13 shows plots of the formaldehyde 22965.7 MHz line at three different power levels. Reasonable straight lines were obtained, particularly considering the potential errors in the mixing process for this system. At a power level of 5 mw, the minimum detectable concentration was estimated to be 0.002 mole percent.

The high adsorption of NH_3 and its high sensitivity caused special problems. In order to dilute the NH_3 sufficiently to determine detection limits, a double dilution was required to

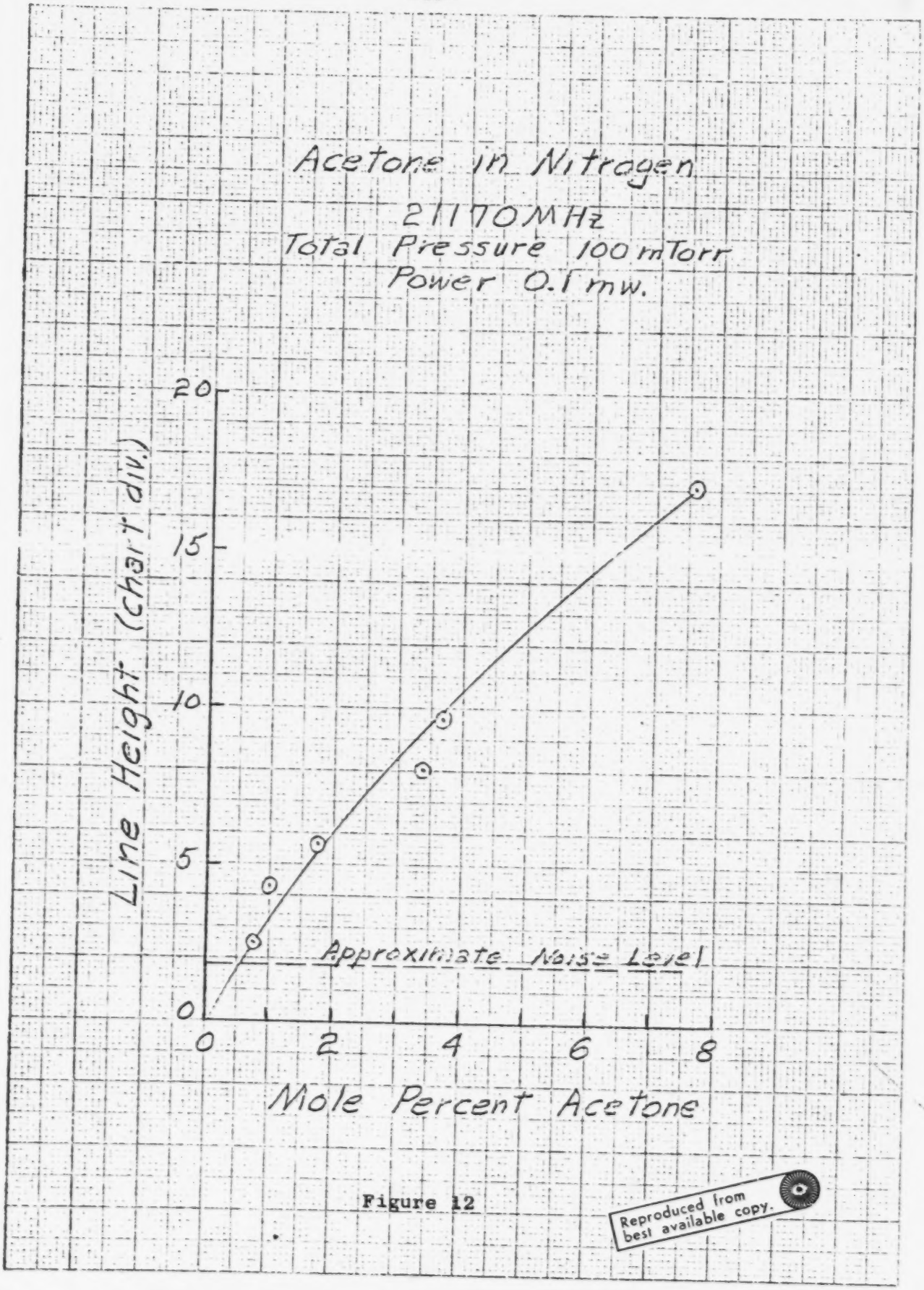

Figure 12

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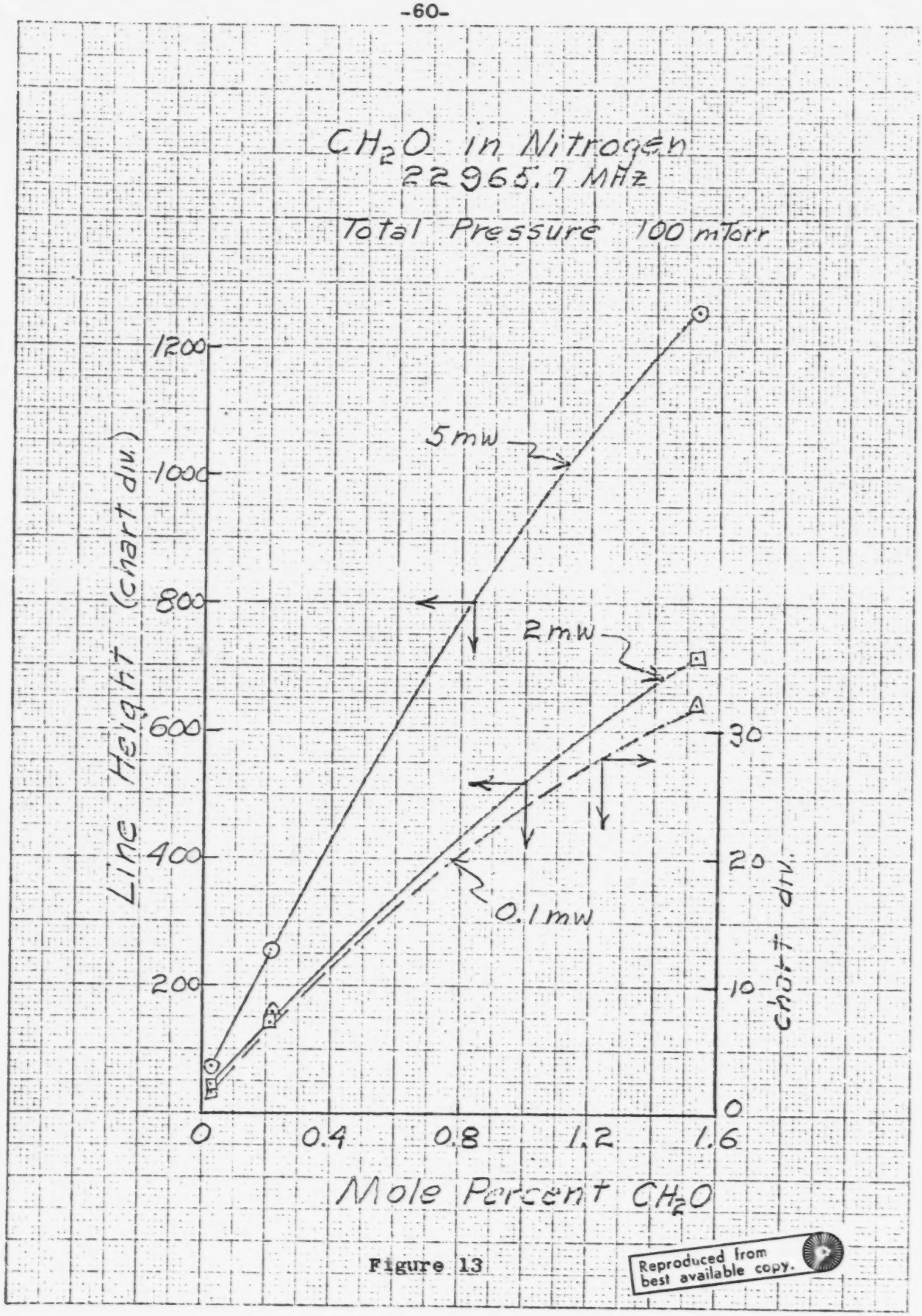

Figure 13

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keep rotameter readings on a usable portion of their scales. Measurements made of equilibrium times indicate that times of the order of 6 to 8 hours are required to completely equilibrate the system. These are only estimates since the long times involved introduced considerable error into our measurements. Figure 14 shows data obtained at a power level of 5 mw. Times allowed for equilibration for each point are also given. This plot is definitely not a straight line because of adsorption problems. The least detectable concentration was estimated to be of the order of 0.002 mole percent at a power level of 5 mw.

One blend of NO_2 at the 0.1 mole % level in nitrogen was studied. This mixture was prepared using the standard rotameter procedure. The mixture was allowed to flow through the plastic tubing for two hours to equilibrate the tubing before admitting gas to the spectrometer. When the mixture was admitted to the spectrometer, a slow increase in the intensity of the 26569.21 MHz line occurred with time. From these data, we estimated that approximately 6 hours time would be required for the line to reach 99% of its maximum intensity. A portion of these data are shown in Figure 15. Our conclusion after a number of attempts to obtain better data is that a microwave spectrometer is practically useless to obtain quantitative results for low concentrations of NO_2. Under strictly controlled conditions, quantitation may be possible, but the effort and time required are excessive. The least detectable concentration is something less than 0.1 mole %.

C. CONCLUSIONS

The results reported above show that the increased complexity of the flow-through system gains very little in the ease and accuracy of handling compounds which adsorb readily on cell walls. Essentially the same results can be obtained by preconditioning the cell through several batch introductions of the same sample.

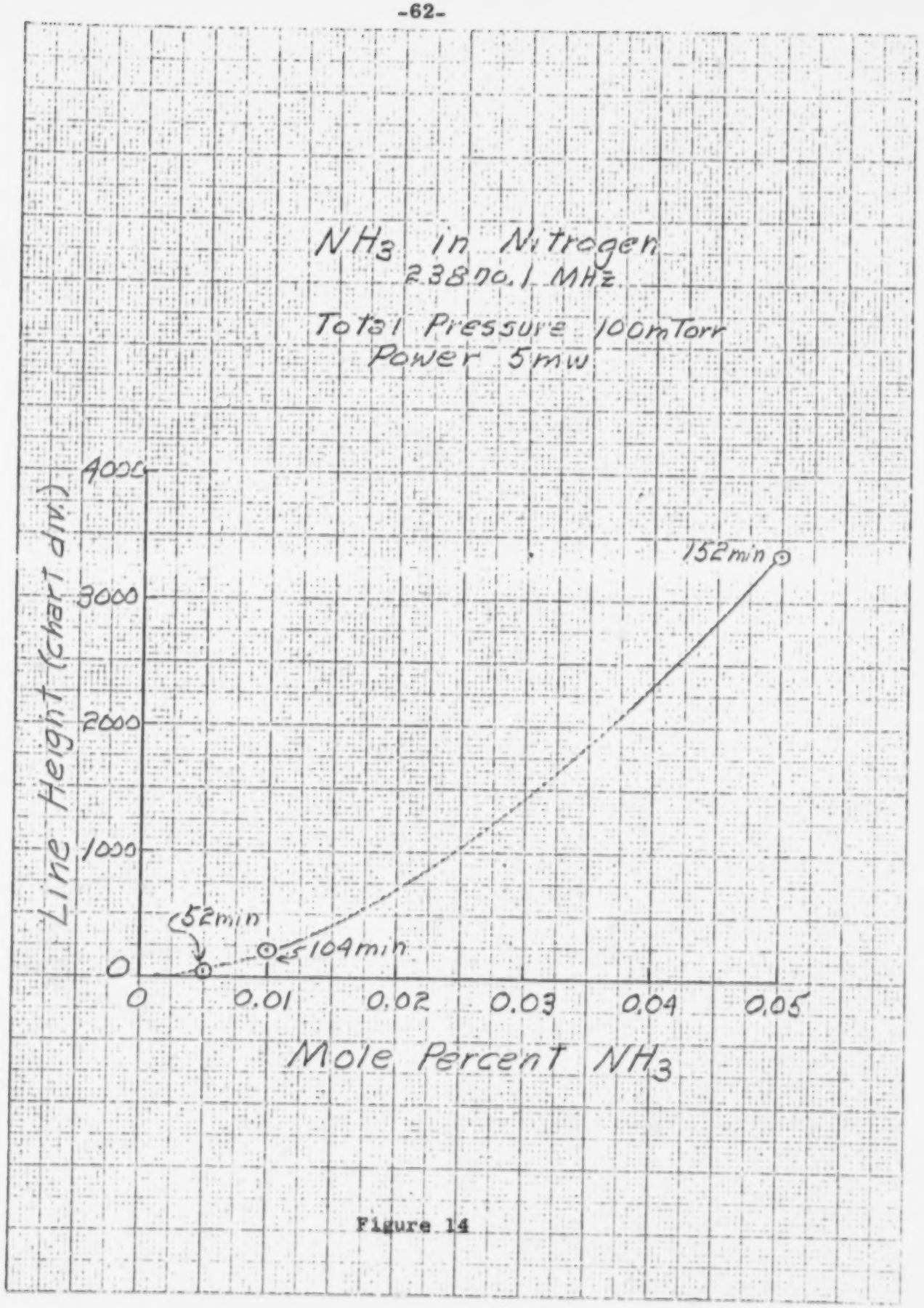
NH3 in Nitrogen
23870.1 MHz.
Total Pressure 100mTorr
Power 5mw
Line Height (chart div.)
4000
3000
2000
1000
0
152min
52min
104min
0
0.01
0.02
0.03
0.04
0.05
Mole Percent NH3

Figure 14

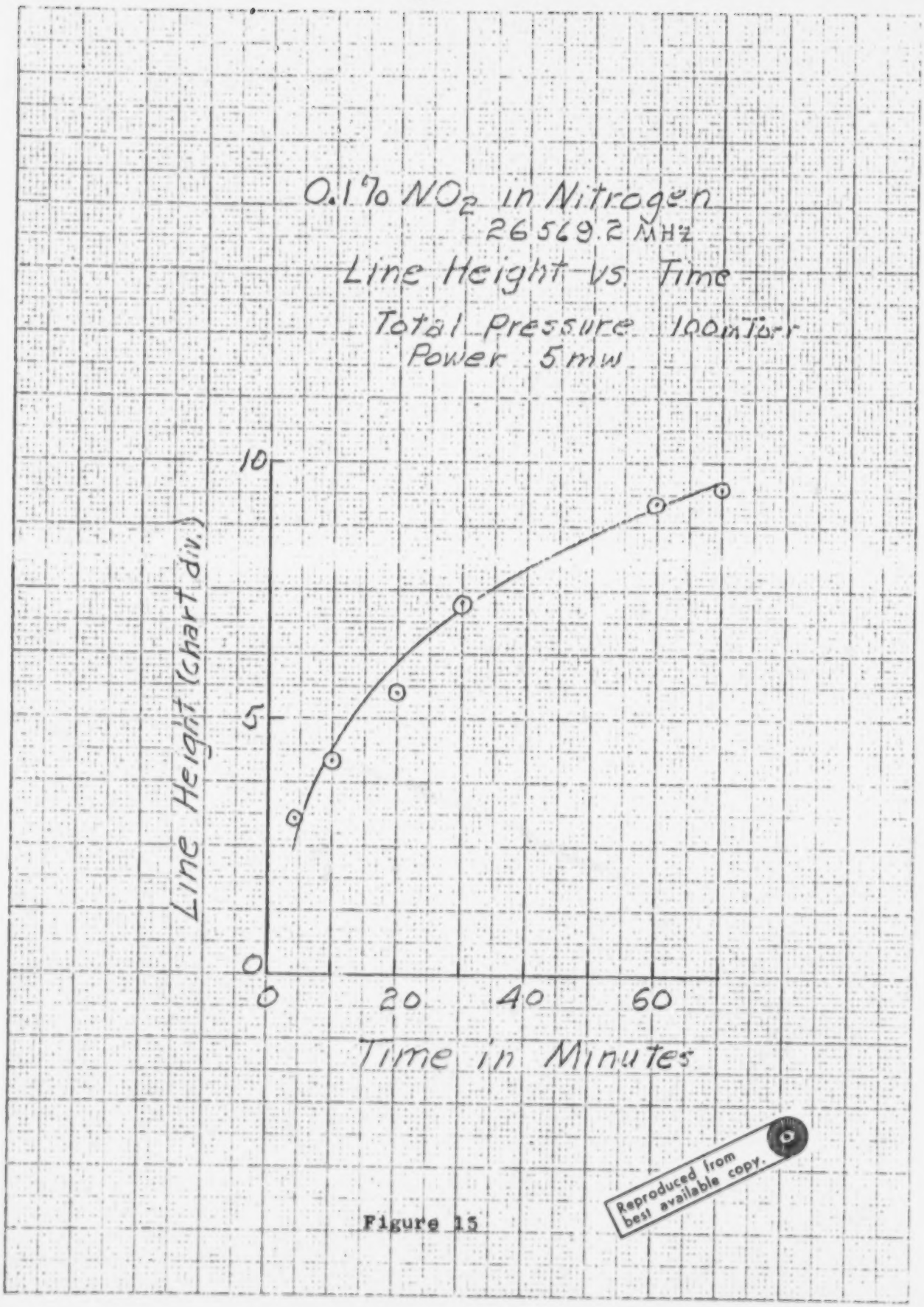

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Figure 15

IX. SUMMARY

Background information and theory, particularly as they apply to analytical applications are presented. Three possible analytical procedures are discussed in some detail. These are the optimum power saturation method, line areas, and line intensities.

The optimum power method has the advantage that the problem of varying line widths is completely eliminated at pressures above some minimum value. It has two important disadvantages: (1) the power level must be optimized for each line and sample pressure encountered, and (2) the amount of power required is well beyond the capabilities of most microwave sources for most molecules. Provisions must be made to operate the crystal detector of the spectrometer so that its output is proportional to the square root of the applied power.

The line area is proportional to the partial pressure of an absorbing molecule and is also independent of the line width. It is however somewhat tedious to measure. We have shown that the product of the line height and the half power width has the same properties as the line area. Measurement is relatively quick and easy. A disadvantage of both area methods is that the scanning rate of the spectrometer must be uniform and repeatable. This was accomplished by locking the frequency of the source to a harmonic of a "tuned" crystal oscillator.

Direct quantitation by means of the line intensity is a very simple and adequate method for certain cases of interest. These include any system in which the desired component is in low concentrations and the composition of the bulk of the mixture is relatively constant. Trace components in air is an ideal system for this method.

The problem of adsorption of gases on the walls of the absorption cell is serious. The amount of such adsorption to be expected was shown by several experiments in which gas pressure was measured as a function of time. Equipment was assembled and a study conducted to determine whether the adsorption problem could be eliminated by a continuous flow-through system. The results indicated that strongly adsorbing compounds can be handled easier through preconditioning of a standard batch cell.

X. CONCLUSIONS

Qualitative and quantitative analyses can be performed on a microwave spectrometer. The outstanding advantage of microwave spectroscopy is the uniqueness of the spectra obtained. For problems which require the positive identification of a compound which has a good microwave spectrum, a microwave spectrometer is very useful. For essentially all other analytical problems, other forms of spectroscopy, such as mass spectrometry and infrared, are faster, cheaper, and considerably more versatile as far as the range of compounds that can be examined. The sensitivity of a microwave spectrometer is not outstanding except for a few compounds like ammonia. Our final conclusion is that for air pollution work a microwave spectrometer should be considered as a very specialized analytical tool to be used only in those specialized cases in which its unique identification ability can be utilized.

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